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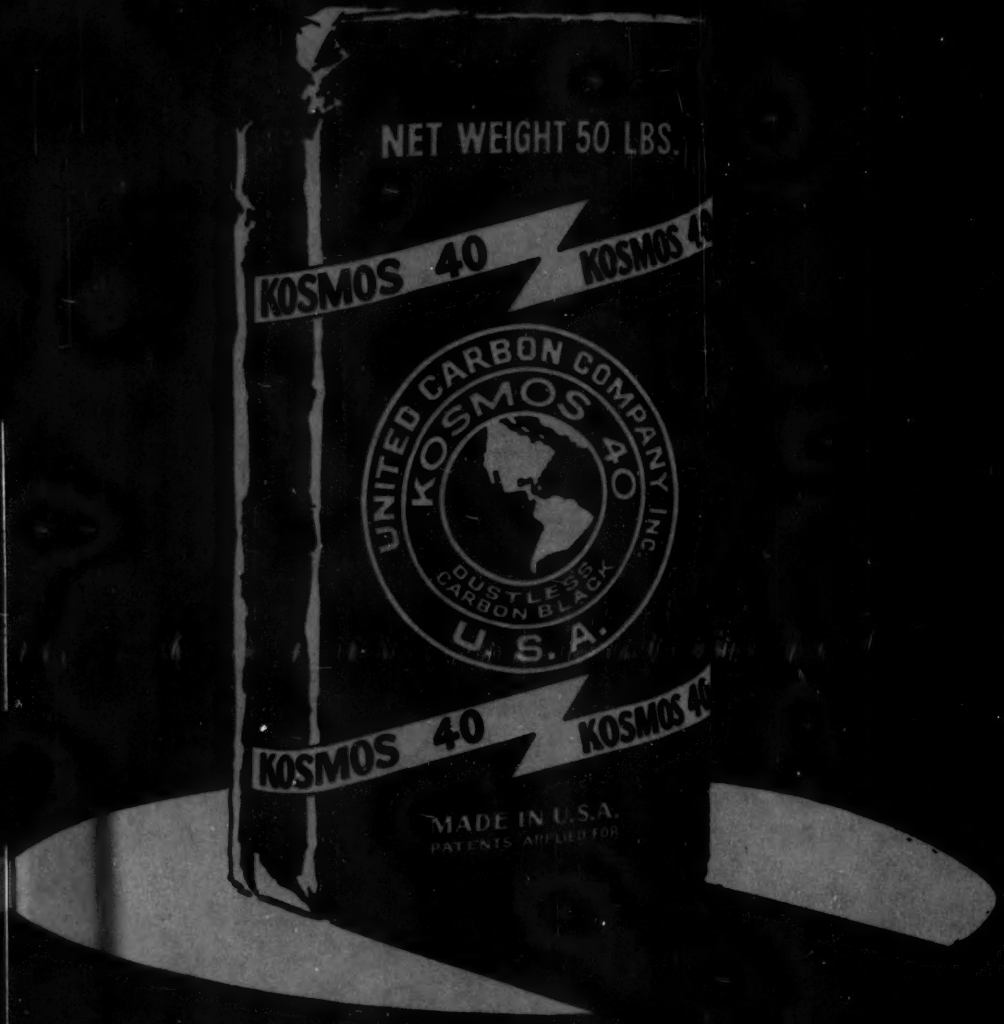


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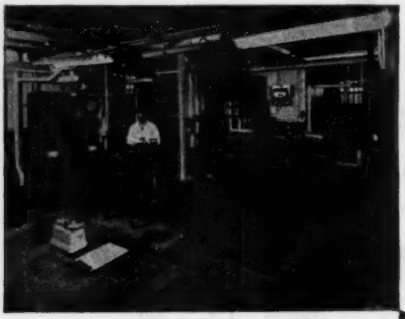

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*One section of constant controlled temperature-humidity testing room showing Scott testers and flexing machine.*

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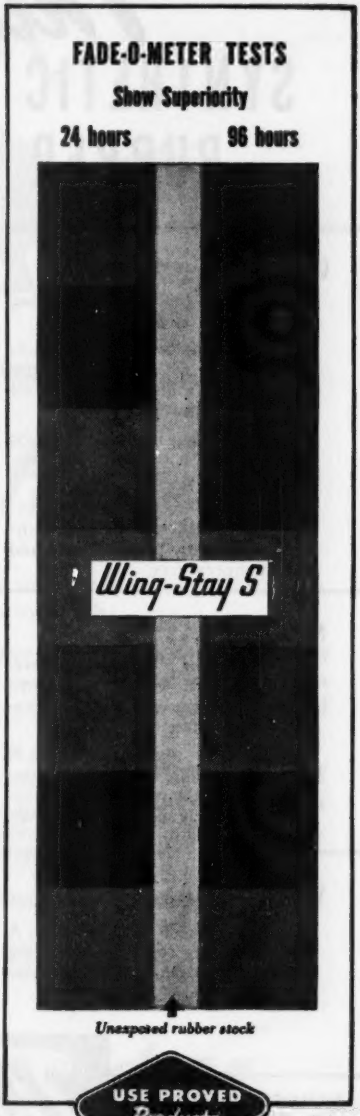


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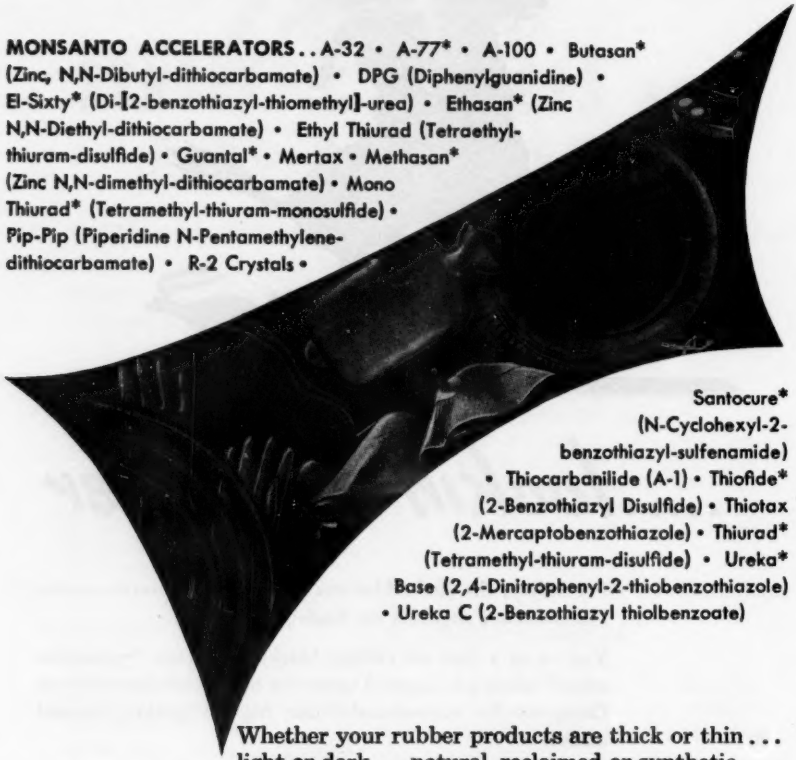

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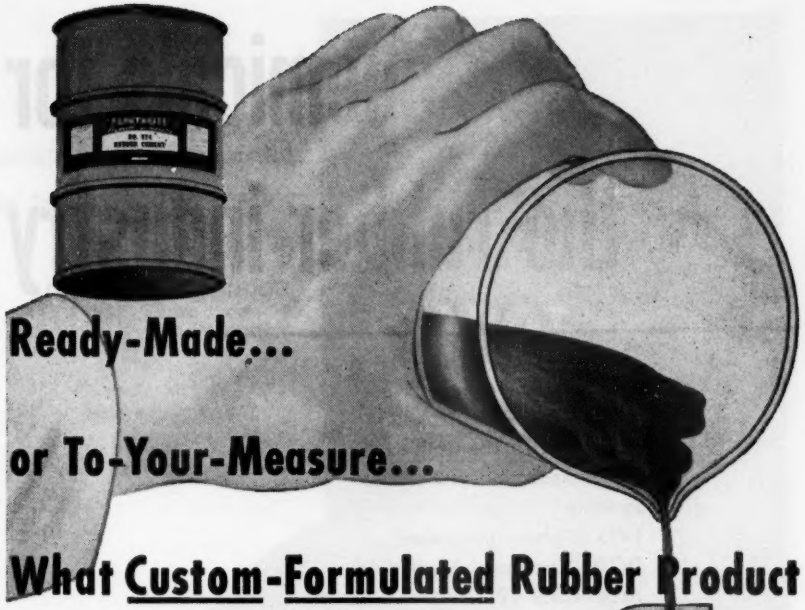

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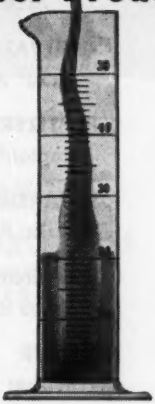

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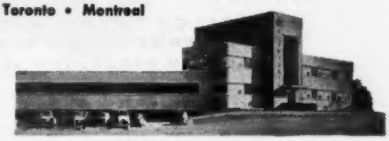

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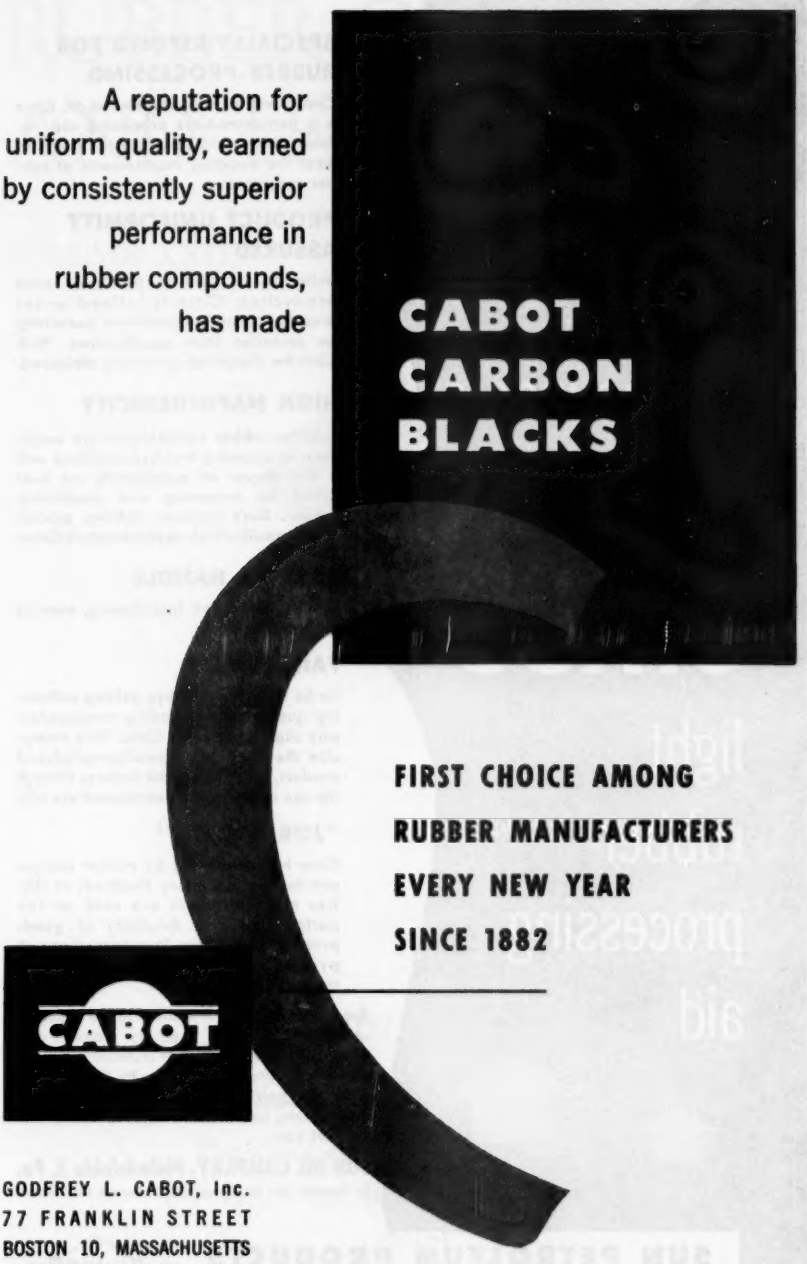


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Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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*Chairman*....D. E. Jones, American Hard Rubber Co., Butler, N. J. *Vice-Chairman*....H. G. Ling, Naugatuck Chemical Division, U. S. Rubber Co., New York, N. Y. *Secretary-Treasurer*....Peter P. Pinto, *The Rubber Age*, 250 W. 57th St., New York, N. Y. (Terms expire December, 1950).

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### Northern California

*Chairman*....F. W. Swain, Pioneer Rubber Mills, Pittsburg, Calif. *Vice-Chairman*....R. R. James, Mare Island Naval Shipyard, Vallejo, Calif. *Secretary*....J. F. Mason, Pioneer Rubber Mills, Pittsburg, Calif. *Treasurer*....G. S. Ramsey, Grove Regulator Co., Emeryville, Calif. (Terms expire December, 1950).

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### Philadelphia

*Chairman*....T. J. Gorman, Quaker Rubber Corp., Philadelphia, Penna. *Vice-Chairman*....H. J. Reid, L. H. Gilmer Co., Division of U. S. Rubber Co.,

Philadelphia, Penna. *Secretary-Treasurer*....T. W. ELKINS, Armstrong Cork Co., Lancaster, Penna. (Expiration of terms not announced).

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RHODE ISLAND

*Chairman*....F. S. BARTLETT, U. S. Rubber Co., Bristol, R. I. *Vice-Chairman*....F. V. NEWMAN, Respro, Inc., Cranston, R. I. *Secretary-Treasurer*....C. L. KINGSFORD, Davol Rubber Co., Providence, R. I. (Terms expire November, 1950).

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SOUTHERN OHIO

*Chairman*....R. B. SUCHER, Inland Manufacturing Division, General Motors Corp., Dayton, Ohio. *Vice-Chairman*....L. J. KEYES, Dayton Rubber Co., Dayton, Ohio. *Secretary*....R. HOSKIN, Inland Manufacturing Division, General Motors Corp., Dayton, Ohio. *Treasurer*....T. C. ARGUE, Inland Manufacturing Division, General Motors Corp., Dayton, Ohio. (Terms expire December, 1950).

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WASHINGTON

*Chairman*....R. J. DEVEREAUX, B. F. Goodrich Co., Washington, D. C. *Vice-Chairman*....T. A. WERKENTHIN, Bureau of Ships, Navy Dept., Washington, D. C. *Secretary*....N. BEKKEDAHL, National Bureau of Standards, Washington, D. C. *Treasurer*....E. A. BUKZIN, Bureau of Ships, Navy Dept., Washington, D. C. (Terms expire October, 1950).

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## SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY BOSTON, MASSACHUSETTS, MAY 23–25, 1949

The fifty-fourth meeting of the Division of Rubber Chemistry was held at the Hotel Statler, Boston, Massachusetts, May 23–25, 1949. The meeting was held separate from the Spring Meeting of the American Chemical Society.

The local committee, composed of J. C. Walton, General Chairman, H. A. Atwater, J. M. Bierer, J. T. Blake, O. J. Brown, Jr., B. H. Capen, J. L. Haas, T. M. Knowland, E. H. Krismann, R. K. Patrick, G. W. Smith, and H. W. Sutton, took care of all arrangements, including visits to the plants of the Boston Woven Hose & Rubber Co., Dewey and Almy Chemical Co., Hood Rubber Co., and Simplex Wire & Cable Co. A clambake was held at Marblehead, at which about five hundred members were present.

At the meeting of the 25-Year Club, with J. M. Bierer presiding, a large silver bowl, in replica of a famous original by Paul Revere now in the Boston Museum of Fine Arts, was presented to A. A. Glidden of the Hood Rubber Company in recognition of his long association of fifty-six years with the rubber industry. W. E. Kavenaugh of the Goodyear Tire & Rubber Company of Windsor, Vermont, received honorable mention for his fifty-one years of service.

The banquet was held at the Hotel Statler, with Chairman Cramer presiding. At this banquet Harry L. Fisher was presented with the Charles Goodyear Medal. Dr. Fisher was introduced by J. T. Blake, who spoke about the

medallist and his career. After presentation of the medal by Chairman Cramer, Dr. Fisher addressed those present on the subject of "Rubber Research and the Need of a Rubber Research Institute in the United States." General George C. Kenney, U. S. Air Force, talked on national defense and the importance of coöperation among the various armed services.

The following papers were presented at four half-day sessions. Papers No. 2 to No. 15 inclusive constitute the Low-Temperature Polymer Symposium.

1. Introductory remarks. H. I. CRAMER, Chairman.
2. Effects of Polymerization Temperature on the Structure of GR-S and Polybutadiene. A. W. MEYER. U. S. Rubber Co., Passaic, N. J.
3. The Effect of Polymerization Temperature on the Properties and Structure of Polybutadienes. PAUL H. JOHNSON. Firestone Tire & Rubber Co., Akron, Ohio.
4. Infrared Analysis of Low-Temperature Polymers. R. R. HAMPTON. U. S. Rubber Co., Passaic, N. J.
5. The Viscosity-Molecular Weight Relation for Polybutadiene. Effect of Polymerization Temperature. R. D. WOLFANGEL AND B. L. JOHNSON. Firestone Tire & Rubber Co., Akron, Ohio.
6. GR-S Latex Polymerized at Low Temperatures. H. S. SMITH, H. G. WERNER, J. C. MADIGAN, AND L. H. HOWLAND. U. S. Rubber Co., Naugatuck, Conn.
7. Use of Alternative Activators in 41°F Polymerization Recipes. H. L. WILLIAMS. Polymer Corporation, Ltd., Sarnia, Ontario.
8. Effects of Temperature of Polymerization of GR-S on the Quality of Tire Tread Stocks. L. M. WHITE. U. S. Rubber Co., Passaic, N. J.
9. Cold Rubber. Its Quality and its Adaptability to Tires. J. H. FIELDING. Goodyear Tire & Rubber Co., Akron, Ohio.
10. Comments on Processing and Tire Service Characteristics of Cold Rubber. I. J. SJOTHUN AND O. D. COLE. Firestone Tire & Rubber Co., Akron, Ohio.
11. Study of Channel Type Carbon Blacks in Low Temperature GR-S. E. M. DANNENBERG AND H. J. COLLYER. Godfrey L. Cabot, Co., Inc., Boston, Mass.
12. Carbon Gel Formation in Cold Rubber. C. W. SWEITZER, W. C. GOODRICH, AND K. A. BURGESS. Columbian Carbon Co., New York, N. Y.
13. Pilot-Plant Preparation of Chemical Rubber by a Continuous Process at Low Temperatures. R. W. LAUNDRIE AND R. F. MCCANN. Government Laboratories, University of Akron, Akron, Ohio.
14. Low-Temperature Polymerizations. Emulsifiers of the Alkyl Aromatic Sulfonate Type. W. W. CROUCH, W. A. SCHULZE, AND C. M. TUCKER. Phillips Petroleum Co., Bartlesville, Okla.
15. Nonaqueous Emulsion Polymerization Systems. EDWARD CARR AND P. H. JOHNSON. Firestone Tire & Rubber Co., Akron, Ohio.
16. Peptization of Low-Temperature GR-S. E. L. STANGOR AND R. R. RADCLIFF. E. I. du Pont de Nemours & Co., Wilmington, Delaware.
17. Physical Evaluation of Foamed Latex Sponge. F. S. CONANT AND L. A. WOHLER. Firestone Tire & Rubber Co., Akron, Ohio.
18. Molding and Casting Processes Using Rubber Latex. S. C. STOKES. British Rubber Producers' Research Association. Welwyn Garden City, England.
19. An Accelerated Weathering Test for Elastomers. W. E. PHILLIPS. B. F. Goodrich Co., Akron, Ohio.

20. Comparison of Some Reclaimed Rubbers. H. A. WINKELMANN. Dryden Rubber Division, Sheller Manufacturing Corp., Chicago, Ill.
21. Hysteresis Determinations with the Goodyear-Roelig Machine. C. S. WILKINSON, JR., AND S. D. GEHMAN. Goodyear Tire & Rubber Co., Akron, Ohio.
22. Constant Stress Method for Elongation of Soft Polymeric Materials. C. A. DAHLQUIST, J. O. HENDRICKS, AND N. W. TAYLOR. Minnesota Mining and Manufacturing Co., St. Paul, Minn.
23. Practical Aspects of Factory Scorch Control. DOUGLAS CHALMERS. Gates Rubber Co., Denver, Colo.
24. New Vulcanization Process Replacement of Zinc Oxide by Use of Oxidizing Agents. B. C. BARTON. U. S. Rubber Co., Passaic, N. J.
25. Comparison of Properties of Butadiene and Isoprene Polymers Prepared by Alfin and Emulsion Processes. J. D. D'IANNI, F. J. NAPLES, AND J. E. FIELD. Goodyear Tire & Rubber Co., Akron, Ohio.
26. Control of Crystallization in Neoprene. L. R. MAYO. E. I. du Pont de Nemours & Co., Wilmington, Delaware.

C. R. HAYNES, *Secretary*

## NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1948. Edited by T. J. Drakeley. Published by W. Heffer & Sons, Ltd., Cambridge, England, for the Institution of the Rubber Industry, 12 Whitehall, London, S.W. 1, England. $7\frac{1}{4}\times9\frac{3}{4}$ in., 108 pp. Price to Members, 4/6 net; Non-Members, 12/6 net.—The latest edition of these specially compiled annual reports covers the technical literature, including patents, for the year of 1948. The same general format of previous editions has been followed, namely, various subjects are covered by leading technologists, all specialists in their respective fields, with extensive bibliographies appended to each chapter. There are twenty-two sections, embracing practically every branch of the rubber industry, together with the usual well handled and cross-referenced author and subject indexes. [From *The Rubber Age* of New York.]

FUNDAMENTALS OF SYNTHETIC POLYMER TECHNOLOGY. By R. Houwink. Published by Elsevier Publishing Co., Inc., 215 Fourth Ave., New York 3, N. Y. $6\frac{1}{2}\times9\frac{1}{2}$ in., 258 pp. $3.75.—This is a completely revised edition of the "Technology of Synthetic Polymers," by the same author, which was issued in 1947. In its present form it is one of the volumes in the current polymer series being issued by Elsevier on the chemistry, physics and technology of high polymeric and allied substances, eight of which have been published to date.

The present volume differs from practically all other works issued thus far on the subject of synthetic polymer technology in that it covers the fundamental background of the chemical and physical factors in the preparation and use of the synthetic polymers including the synthetic rubbers and polymers based on natural rubbers (rubber derivatives). Moreover, it suggests solutions to some of the many problems which arise in manufacture.

Coördinating researches and results of both European and American workers, the book includes a comprehensive discussion of the properties and of the structural formulas of all the chief groups of industrial plastics. Included in this group are polymers based on ethylene and its derivatives, phenol and

aniline, carbamides, carboxylic acids, cellulose, proteins, etc. One chapter is devoted to silicones.

The chapter on "Synthetic Rubbers" has sections covering the manufacture of butadiene, styrene, acrylonitrile, chloroprene, isobutylene, ethylene polysulfide, and silicones. It also discusses polymerization and further manufacturing processes and the properties of the finished products. Among the materials covered in the chapter on "Polymers Based on Natural Rubber" are chlorinated rubber, rubber hydrochloride, oxidation products, rubber isomers, and other rubber derivatives.

The book has 16 chapters in all. [From *The Rubber Age* of New York.]

COLLOID SCIENCE. VOL. II. REVERSIBLE SYSTEMS. Edited by H. R. Kruyt. Printed in the Netherlands. Available from Elsevier Publishing Co., Inc., 215 Fourth Ave., New York 3, N. Y. 6¾×9¾ in., 754 pp. $11.50.—Recognizing the need for a collective work on the science of colloids, the editor of this work began preparations for its publication before World War II. The original intention was to secure contributions from noted colloid scientists throughout the world, but because of the exigencies of war it was finally restricted to contributions from Dutch technologists.

Although there was some question in the minds of the contributing group as to whether "colloid science" is an adequately definable concept, it was finally determined to use this title on the ground that colloidal systems are characterized by their possession of large kinetic units. Further, since there is continuity between the behavior of large and small kinetic units, there are sufficiently salient differences between the extremes to divide the treatment of the subject without losing sight of the connections.

Based on this reasoning, the present work has been divided into two volumes, one devoted to irreversible systems and the other to reversible systems. Through accidental circumstances Volume II, devoted to the reversible systems, has been completed earlier than Volume I and has been published first. The data are too extensive for critical review, and accordingly we are merely listing the 14 separate contributions below:

(1) A survey of the study objects; (2) Formation and structure of macromolecules; (3) Thermodynamics of long-chain molecules; (4) Physical properties of randomly kinked long-chain molecules; (5) Determination of the molecular weight of macromolecules; (6) Macromolecular sols without electrolyte character; (7) Sols of macromolecular colloids with electrolytic nature; (8) Crystallization, coacervation and flocculation; (9) Reversal of charge phenomena, equivalent weight and specific properties of ionized groups; (10) Complex colloid systems; (11) Morphology of coacervates; (12) Gels; (13) Solid macromolecular systems with one (chemical) component; (14) Association colloids.

Contributors include H. G. Bugenberg de Jong, R. Houwink, J. J. Hermans, P. H. Hermans, J. Th. G. Overbeek, and H. L. Booij. [From *The Rubber Age* of New York.]

ANNOTATED COMPREHENSIVE LIST OF TRADE NAMES OF SYNTHETICS. Compiled by T. R. Dawson and M. J. Thomsett. Issued by the Research Association of British Rubber Manufacturers, 105-7 Lansdowne Road, Croydon, England. 8×13 in., 230 pp. Mimeographed. $10.00.—The troublesome problem of trade names which faces the entire chemical industry, including the rubber and plastics fields, will be considerably eased by this comprehensive

collection of about 8,000 entries, which represents a search of every journal, book, and trade name list in the large R.A.B.R.M. library of rubber and plastic literature from June 30, 1926, through July 31, 1949. The work comprises a single alphabetical list of substitutes and extenders for natural rubber, synthetic rubbers, and synthetic resins and plastics, with the compilers giving a broad interpretation to those terms. Wherever possible, the nature or chemical composition and the form in which the synthetic is available are given, in addition to the name and address of the manufacturer or distributor. Names included are not only registered trade marks, but also commercial and technological terms such as rayon, nylon and Neoprene. The R.A.B.R.M. is to be congratulated for undertaking this valuable compilation. [From *The Rubber Age* of New York.]

DIRECTORY OF BRITISH RUBBER MANUFACTURERS AND PRODUCTS. 1949 Edition. Federation of British Rubber Manufacturers' Association, 43 Bedford Square, London W.C.1, England. 288 pages.—This comprehensive, illustrated directory of the British rubber industry consists of five sections. The first section lists manufacturers and their addresses and the names, addresses, and products of their overseas distributors. The second section consists of a classified list of rubber products and their suppliers; while the third section contains advertisements and catalogs of the various companies. The British tire industry and its members are covered in the fourth section, and the concluding section gives a list of trade names and trade marks. Descriptive material and lists appear in English, French, and Spanish. Copies of this directory are available for consultation by interested firms at the principal British consulates in the United States. [From the *India Rubber World.*]

REVIEW OF CURRENT RESEARCH AND DIRECTORY OF MEMBER INSTITUTIONS, 1949. Engineering College Research Council, American Society for Engineering Education. Paper, 6 by 9 inches, 186 pages. For sale by F. M. Dawson, College of Engineering, State University of Iowa, Iowa City, Iowa. Price, $1.75.—This edition presents classified listing and brief description of more than 4,000 current college and university research projects in engineering subjects. Entries cover 82 institutions and give information on administrative policies on research, expenditures, personnel, courses and conferences of special interest, and titles of research studies currently active. [From the *India Rubber World.*]

STANDARDS ON TEXTILE MATERIALS. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6×9 in., 586 pp. $4.50.—This edition includes 84 specifications, test methods, and tolerances developed by A.S.T.M. Committee D-13 on Textile Materials, as well as considerable other related material. Of the standards, 23 cover cotton, 9 rayon and silk, 11 wool, 7 asbestos, 6 glass, and 5 come under the heading of bast and leaf fibers. The balance of the standards are general testing methods, etc., covering testing machines, fire-retardant properties, air permeability of fabrics, interlaboratory testing, etc. Also included are a psychometric table for relative humidity, photomicrographs of common textile fibers and of defects in woven fabrics, a convenient yarn number conversion table, a glossary of textile terms, and terms relating to hand of fabrics. There are also convenient tables of contents (by subject and by A.S.T.M. designation) and an index of methods of tests. [From *The Rubber Age* of New York.]

SCIENTIFIC AND TECHNICAL ABBREVIATIONS, SIGNS, AND SYMBOLS. By O. T. Zimmerman, Professor of Chemical Engineering, University of New Hampshire, and Irvin Lavine, Formerly Professor of Chemical Engineering and Head of the Department, University of North Dakota. Industrial Research Service, Dover, N. H., 1948. xii+476 pp. Illustrated. 14×22 cm. Price, $7.50.—In the days of Berzelius and Bunsen a scientist carried most of his science in his head and usually knew where to find the rest easily, but the time for abstract journals soon came, then science dictionaries, encyclopedias, monographs and special compilations such as the one here considered. Zimmerman and Lavine have done an extensive job of collecting the abbreviations, signs, and symbols from A (aeronautics) to Z (zoölogy), with chemistry, physics, biology, botany, astronomy, mathematics, engineering, radio, electronics, hydrography, topography, meteorology, medicine, communications, machine and tool shopcraft, commerce, banking, military, navy, even plumbing and heating, in between, all well arranged by subjects and fields, in neat and readable tables. The sources are many, in particular the American Standards Association.

Any criteria of excellence or completeness are hard to establish; the reviewer could not find the kX. unit now substituting for Å. (A. U.), nor $[\alpha]^t_D$, nor $MR_D$, all of which are commonly used by chemists, nor O. R. C., B. R. T. or B. L. E. in the section devoted to railway terms. The authors discuss favorably in the Preface the growing practice of omitting periods after abbreviations. The reviewer and most chemists have not succumbed to the infection as yet; there are points in its favor, superfluity of the period, and the space it fills, but equally as good or better arguments against. The space filled by the period is seldom responsible for an extra line, and the confusion produced, the décolleté appearance of the abbreviation, the difference between an abbreviation and a symbol, the secretarial problems involved in preparing uniform copy for publication, all these are effective *contra* points. Even the strong advocates cannot agree on how far to go and none of them are 100 per-cent-ers. The writers have succeeded quite well in their aim "to make available in one convenient volume the principal abbreviations, signs and symbols used in a number of scientific and technical fields". [A. D. Bliss in the *Journal of The American Chemical Society*.]

CHEMICAL ENGINEERING CATALOG, 1949–50. Thirty-Fourth Edition. Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth, 8½×11 inches, 1580 pages.—This edition of the Catalog, although showing a decrease of 187 pages from the preceding issue, continues to offer comprehensive directory information on equipment and engineering materials for the process industries. The format corresponds to previous editions and consists of an alphabetical index of firms represented, a trade name index, a classified index, and section comprising manufacturers' catalogs. [From the *India Rubber World*.]

LES DÉRIVÉS CHIMIQUES DU CAOUTCHOUC NATUREL [Chemical derivatives of natural rubber]. J. Le Bras (Directeur du Centre de Recherches de l'Institut Français du Caoutchouc) and A. Delalande (Institut Français du Caoutchouc). Preface by Jacques Duclaux (Professor at the Collège de France). Dunod, Paris, 1950. xxiv+485 pp., 37 tables and 47 figures, 13.5×21.5 cm.—This is the first book devoted only to "The Chemical Derivatives of Natural Rubber" and, fortunately for those readers in this field, it is very well done. The authors

have spared no pains to make the coverage of the scientific and patent literature complete and the treatment understandable. Work that is described only in isolated articles, patents, and special chapters in treatises on rubber is gathered together in a well organized manner and discussed in a clear and interesting fashion. The authors discuss the methods of preparation, chemical structure, and the chemical and physical properties of the derivatives and, where the derivatives are of industrial importance, they give adequate accounts of the methods of manufacture and application. The book can be used as an excellent reference book without its having the semblance of an encyclopedia. A brief introductory chapter on the origin, constitution, and chemical properties of natural rubber precedes the main portion of the book. Then two chapters, which take up approximately one-half of the entire book, follow on the halogen and hydrohalogen derivatives. The second half includes the work on hydrogenated rubber, oxygen and cyclized derivatives, special derivatives and modified rubbers. In each chapter there is a good balance in the handling of the scientific and any industrial aspects of the different substances, and detailed descriptions that show the authors' thorough acquaintance with the published material. The book contains many photographs, diagrams, tables, and structural formulas, all of which add to the usefulness of the book. The numerous literature and patent references are given at the end of each chapter. That the coverage of the subject is, no doubt, complete is indicated by the number of references, for example, 510 for halogen derivatives, 230 for hydrohalogen derivatives, and 299 for cyclized derivatives. Dates of references in 1948 were noted. The table of contents covers 10 pages and the unusually fine index covers 34 pages. It is regrettable that the authors have not included derivatives from synthetic elastomers also. Such an addition would have added to the value of the book. The book is well printed on good glossy white paper, and has a heavy paper cover. Typographical errors are practically absent. This book bears the imprint of authors who are enthusiastic about their subject; it should be a real stimulus to others working in, or desirous of, working in this field.

HARRY L. FISHER

# GIUSEPPE BRUNI
## 1873–1946

PHILIP SCHIDROWITZ

EALING, LONDON W5, ENGLAND

Giuseppe Bruni, a pioneer in the development of structural chemistry and the chemistry of solid solutions and isomorphism, and also outstanding for his researches in the chemistry and technology of rubber, was born in Parma, Italy, in 1873, and died in Milan in 1946. The news of Bruni's passing did not, for some unexplained reason, become known to most of his many friends and admirers abroad until the end of 1949.

After graduating in Parma in 1896, he joined the renowned Ciamician at Bologna University, where for nearly ten years he worked mainly on the nature and theory of solid solutions and of isomorphism. In 1908, he summed up his researches in this field in a monograph entitled "Solid Solutions and Isomorphism," published in Germany under the title "Feste Lösungen und Isomorphismus." He temporarily left Bologna to work with van't Hoff in 1900–1901, and the latter subsequently emphasized the importance of Bruni's researches in the following words:

"Ce savant à contribué d'une partie prépondérante à l'adoption des lois sur les solutions solides et les mélanges isomorphes, qui, sans son intervention auraient été troublée par des notions confuses." [This scholar and master has contributed in a major way to the establishment of the laws of solid solutions and of isomorphic mixtures, for without the part which he played, the formulation of these laws would have been beset by a confusion of ideas.]

The year 1907 saw Bruni appointed to the Chair of General and Inorganic Chemistry at Padua, where for a decade he conducted researches on diffusion in the solid state, on the cryoscopic method, etc. In 1917 he was appointed Professor of General and Inorganic Chemistry at the Polytechnic School of Milan—an institution similar in character to the Massachusetts Institute of Technology. He held this post until shortly before his death.

In the following, a brief résumé is given of his work in rubber science and technology.

### RESEARCHES ON ACCELERATORS AND VULCANIZATION

Bruni's many researches in connection with rubber science and technology included work on the theory of vulcanization, on accelerators and acceleration, on the chemical and physical properties of raw rubber, on the chemistry and structure of the rubber hydrocarbon, on aging, on latex problems, and on the production of carbon black.

*Theory of Vulcanization.*—Using a compound containing a powerful accelerator, Bruni found, by extrapolation of the combined sulfur-modulus curve, that the zero load corresponded to about 0.15 per cent of combined sulfur, and came to the conclusion that vulcanization may be regarded as commencing only after this percentage of combined sulfur has been reached. This finding suggested that, since strong rubbers can be produced which contain only a very

small proportion of combined sulfur, the vulcanization reaction may involve substitution.

*Accelerators and Acceleration.*—Bruni undoubtedly was the first to publish work on ultra-accelerators (see Italian patent 173,322 (1918)). This work started with research on the activity of the metallic salts of dithiocarbamic acid. Furthermore, Bruni and Romani were the first to discover "sulfurless" vulcanization, *i.e.*, that certain organic substances containing bound sulfur (dipentamethylene disulfide was the original compound examined) are able to effect cures without the addition of sulfur as such. This gave rise to the disulfide theory of vulcanization, which aroused widespread discussion, in which Bedford and Sebrell, Whitby, and others took part, especially in regard to the method of action of mercapto accelerators.

Independent of Bedford and Sebrell in the United States, and at about the same time in 1921, Bruni "discovered" mercaptobenzothiazole (generally known as MBT), probably the most useful general-purpose accelerator yet discovered, and which, after nearly thirty years, has not lost much of its popularity.

In the same year (1921) Bruni also found what was at the time described as a new "cold" cure, and here again, workers in the United States (Bedford and Scott) seem to have been working independently on much the same subject, although Bruni may have been a few months earlier as regards date. Bruni's "cold" cure consisted essentially of incorporating an amine and zinc oxide in a mix, and then exposing the mix to the action of carbon disulfide. Bruni started from aniline, whereas the United States workers' experiments were based on piperidine. The point of all this was, for example, in the case of the aniline-carbon disulfide reaction, that formation of the accelerator *in situ* gave a more active cure than when the accelerator as such, for example, in Bruni's case thiocarbanilide, was incorporated on the mill.

### CHEMICAL AND PHYSICAL PROPERTIES OF CRUDE RUBBER. STRUCTURE OF HYDROCARBON

In connection with his voyages to the rubber plantations shortly after World War I, Bruni found small quantities of manganese in some plantation rubbers, and was able to connect this fact with the inferior quality of some of these crude rubbers. The composition of "slab", *i.e.*, "maturated" rubber, was also examined by him, and he was able to identify a number of its water-soluble components.

Coming to Bruni's work on the physical properties of rubber, $x$-ray research was a matter of much interest to him, and he established at the Milan Polytechnic School what was, probably, the first laboratory in Italy suitably equipped for this type of work. Further, using electron beams in the study of crystalline structure instead of $x$-rays, Bruni and Natta studied the beam pattern of unstretched raw rubber and developed a new method for obtaining the extremely thin films required in this work. This electron beam work was the first of its kind, and it led him to adapt the technique of electron diffraction for the purpose of detecting molecular groupings in unstressed sol rubber. He associated himself with those who came to the conclusion that the units of the rubber hydrocarbon are joined by primary valences.

The quality of Bruni's scientific work will be obvious from the above brief summary; some measure of the extent of his researches may be gathered from the fact that in Bedford and Winkelmann's "Systematic Survey of Rubber Chemistry" (published 1923) there are eleven entries relating to Bruni's work,

and in Davis and Blake's "Chemistry and Technology of Rubber" (1937) there are no fewer than twenty-two entries.

*Technology.*—Bruni's fundamental work on accelerators attracted the attention of the Pirelli firm, and it was during the first World War that he commenced his long connection with the Milan company—first as consultant, and later as chief of the research laboratories—which was to continue until his retirement in about 1943. But Bruni's work was not confined to the laboratory; the application of the results of research to industry, patent law and litigation, and other matters of practical import interested him, and benefited by his interest. Thus, he was concerned in the production of carbon black from materials other than natural gas, and read a paper on this subject at the Rubber Technology Conference in London in 1938. He did brilliant work in connection with patent technique and legislation, and published a series (1935–41) of papers on patent law, strongly urging, *inter alia*, that anterior publication in scientific or technical publications should not deprive an inventor of the right to apply for patent protection.

The writer had many opportunities to become acquainted with Bruni's skill and knowledge in patent matters; indeed, his first coming together with him in the early thirties was in this field. Recognition of Bruni's status in patent matters led to his becoming a member of the Board of Directors and, later, Chairman of International Latex Processes.

It is not remarkable that a man of Bruni's stature received many honors; among these one may mention that he was the recipient of the King's Prize for Chemistry (awarded by the Academia dei Lincei) in 1913; in 1924 the American Chemical Society elected him an Honorary Member (the only Italian to have received this distinction) after he had been a Member since 1912. Similarly, the (British) Institution of the Rubber Industry, after a membership of two years, elected him a Fellow in 1928. In 1929 he was elected to the Italian Chamber of Deputies as a representative of the universities, and later was nominated a Senator.

The writer's many contacts with Bruni over some fifteen years—in London, Paris, Milan; in the factory; in the conference hall; at private gatherings—and much correspondence on scientific and technical matters, led him (the writer of this note) to appreciate Bruni's sterling qualities as a man, and his high intellectual qualities in scientific and other fields of thought. He was equally fluent in English, French, and German, and of wide culture.

Bruni retired, says Rollier, to strictly private life in 1943, but he (Rollier) "received many demonstrations of his sympathy for the new birth of democracy in his country."

The writer cannot from personal knowledge speak of the impact of the events of the last few years of Bruni's life on the man, but Rollier (writing from the Polytechnic School of Milan) in the *Journal of the American Chemical Society* of February, 1949, pages 382–384, said:

"Bruni's participation in the public life of his country . . . was to end in sheer bitterness because, owing to his awareness and acute sense of responsibility, he foresaw the outcome of many absurdities he was witnessing, but was unable to avail against them because his spirit of tolerance and moderation went unheeded in that tragic period."

# THE DEGREE OF CRYSTALLINITY IN NATURAL RUBBER.* III. CORRELATION BETWEEN X-RAY AND DENSITY MEASUREMENTS

J. J. ARLMAN

LABORATORIUM VOOR TECHNISCHE PHYSICA DER TECHNISCHE HOGESCHOOL, DELFT, HOLLAND

## INTRODUCTION

The $x$-ray study of the crystal structure of rubber dates from the discovery by Katz[1] in 1925 that stretched rubber gives an $x$-ray fiber pattern. This proves the possibility of alignment of the long rubber chains and the formation of highly ordered regions. The regions giving rise to the fiber pattern of stretched rubber and the Debye-Scherrer rings of unstretched frozen rubber are called crystallites.

Several different unit cells have been suggested during the last twenty years to account for the fiber pattern. The different unit cells and the calculated density are listed in Table 1.

TABLE 1

| Author | Year | Symmetry | $a$ in Å | $b$ in Å | $c$ in A fiber axes | $\beta$ | Density |
|---|---|---|---|---|---|---|---|
| Mark and von Susich[3] | 1928 | orthorhombic | 12.3 | 8.3 | 8.1 | | 1.07 |
| Lotmar and Meyer[4] | 1936 | monoclinic | 12.65 | 8.54 | 8.20 | 83°20′ | 1.02 |
| Sauter[5] | 1937 | orthorhombic | 12.6 | 8.91 | 8.2 | | 0.97 |
| Mörss[6] | 1938 | orthorhombic | 12.4 | 8.9 | 8.15 | | 1.00 |
| Misch and von der v.d. Wijk[7] | 1940 | orthorhombic | 25.2 | 8.97 | 8.20 | | 0.97 |
| Bunn[8] | 1942 | monoclinic | 12.46 | 8.89 | 8.10 | 92° | 1.00 |

The several unit cells are based on different interpretations of the $x$-ray fiber diagram. Though density measurements had already been carried out in 1929 by van Rossem and Lotichius[2] the true density of the crystallites was unknown due to the fact that in every specimen there remains an amorphous portion. So the density could only afford a rough check of unit cell dimensions. The unknown degree of crystallization in the rubber formed the missing link.

Now Goppel[9] worked out an $x$-ray method to determine the degree of crystallization. However, his results on crude rubber, combined with density measurements, do not agree with the density of the crystallites calculated from the cell of Bunn. As there were good arguments in favor of the cell of Bunn, the author decided to examine again the $x$-ray method of Goppel. The following paragraph deals with the description of the experiments.

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## DISCUSSION OF THE X-RAY METHOD TO DETERMINE THE DEGREE OF CRYSTALLIZATION

*Frozen raw rubber.*—For frozen raw rubber the $x$-ray method of Goppel is based on the photometer record[10] of a special region of the $x$-ray diagrams. In this region there are no reflections, and the diffraction angle, increasing from 5°40′ to 12°30′, is much beyond the small angle scattering range. The scattering in this region is due to: (1) coherent scattering of all wave lengths; (2) incoherent scattering; (3) scattering of the air traversed by the primary beam.

Goppel examined the influence of the white radiation by reducing the anode tension of the $x$-ray generator and got the impression that the influence was negligible. The present author examined the effect in an independent and direct way by means of an exposure at normal tension (40 kV peak voltage) but with two films in the plate holder separated by an aluminum filter of thickness 0.325 mm. This filter absorbed 99 per cent of the copper characteristic radiation but only a small fraction of the white radiation. After correcting for the air scattering, the photometer curves of the two films are compared.

In this way the author found that the scattering of the white radiation in the region mentioned above is not negligible and amounts to 50–30 per cent of the total scattering. In his opinion the absence of the influence of the anode voltage found by Goppel must be ascribed to nonessential causes.

The intensity on the second film, which is the sum of coherent and incoherent white radiation scattered by the sample, turned out to be in practice, independent of the degree of crystallization as could be concluded from photometer records of several $x$-ray diagrams.

The uncorrected results of polychromatic measurements of the degree of crystallization are too small by a factor 1.5 or 2. This factor is not constant, but varies with the diffraction angle and the voltage applied to the generator.

So the author decided to use monochromatic rays from a pentaerythrite crystal. The incoherent scattering from the rubber is then still present, but the correction can be derived from the results of the investigation carried out by Simard and Warren[11] on smoked sheet rubber. They made a monochromatic exposure of amorphous smoked sheet, avoiding the air scattering by evacuating the camera. From the resulting intensity curves it is possible to calculate the ratio $\alpha$ of the incoherent to the total scattering for every value of $\theta$. This ratio increases from 0.12 to 0.15 in the region used to determine the degree of crystallization. The corrected value of the degree of crystallization $K$ can be derived from the uncorrected value $K'$ by means of the relation:

$$K = \frac{K'}{1 - \alpha}$$

This relation is easily proved to be correct by remembering that, properly speaking, Goppel's $x$-ray method determines the percentage of amorphous rubber in the sample. The maximum relative error in this percentage is about 5 per cent. When the degree of crystallization is about 30 per cent, the relative error in this percentage is about 10 per cent.

*Stretched rubber.*—In the case of stretched rubber the $x$-ray method of Goppel uses naturally the maximum of the amorphous halo. Working with polychromatic radiation, the influence of the white radiation is not so large as before in the case of frozen raw rubber. The ratio between the intensity caused by the continuous spectrum and the total intensity is 1:7 when the generator

is operated at normal tension. Thus the influence of the white radiation is 2 or 3 times less than in the former case.

At the maximum of the amorphous halo, the influence of the incoherent scattering of the characteristic radiation by the sample is less too. The ratio of the incoherent to the coherent scattering of the CuK $\alpha$ radiation is 0.06.

From these ratios the following formula can be derived:

$$A = \frac{A' - 0.18}{0.82}$$

$A'$ is the amorphous part of the rubber, calculated without correction, and $A$ is the corrected value. It follows that the difference between the uncorrected and the true amount of crystalline rubber, $K' = 1 - A'$ and $K = 1 - A$, respectively, is $K - K' = 0.22\ K'$.

The highest degrees of crystallization $K'$ in stretched rubber, determined by Goppel without any correction, were about 30 per cent. Hence the corresponding corrected values $K$ are about 37 per cent. So the gap between the results of Field[12] and Goppel is not removed by the present author's improved interpretation of the $x$-ray diagrams. His results differ considerably from those of Field and are in complete agreement with the results of Goppel's thesis.

## DENSITY MEASUREMENTS

Density measurements were carried out on the same rubber used for the $x$-ray measurements. They were performed by two methods by using a pyknometer as well as by weighing the rubber under water.

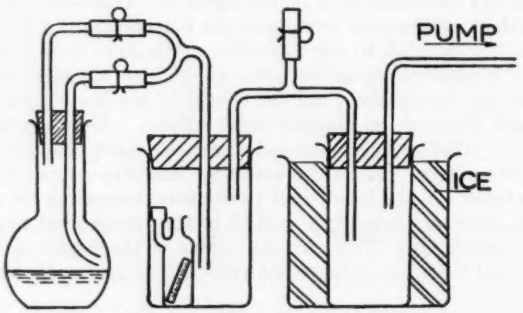


FIG. 1.—Sketch of apparatus for density determinations.

The pyknometer was filled with distilled water in such a way as to avoid air bubbles on the surface of the rubber. The principles of the method are described by Hermans[13].

The experimental arrangement was altered somewhat so as to fill the pyknometer with water of room temperature, at which all investigations were carried out. A sketch is given in Figure 1.

About 3 grams of rubber in five or six pieces were used, and all normal corrections were made.

The degree of crystallization was computed assuming the density of the crystals to be given by the cell of Bunn. The relative error in the densities obtained was 0.05 per cent. The resulting relative error in the degree of crystallization amounts to 5 per cent.

Out of the sheet of rubber several samples were cut and used to determine the degree of crystallization by the $x$-ray method and by density measurement. Every determination was repeated a number of times, and from the results a mean value was obtained. The results obtained by weighing under water agree very well with the results obtained with the pyknometer.

## COMPARISON OF THE RESULTS OF X-RAY AND DENSITY MEASUREMENTS

The investigations were carried out on smoked sheet and crepe rubber. The results are listed in Table 2.

The correlation between the results of polychromatic measurements and the other determinations is a very slight one, probably because of the fact that the intensity distribution of the generator used is not constant. In the last two columns the mean values with the corresponding probable error derived in a statistical way from measurements are given. The agreement between monochromatic $x$-ray and density measurements is very good. Assuming the unit cell of Bunn to be correct, it can be inferred that the two concepts of crystallinity as defined by $x$-ray and by density measurement are identical. This would be a strong argument in favor of the absence of regions with intermediate structure.

TABLE 2

| Number of the rubber | Type of rubber | Age in years | Polychromatic $x$-ray measurement | | Monochromatic $x$-ray measurement | | Density measurement $K = 1{,}00$ | |
|---|---|---|---|---|---|---|---|---|
| | | | $K$ % | $N$*) | $K$ % | $N$ | $K$ % | $N$ |
| *R* 71 | smoked sheet | 32 | 18 | 28 | 36.6±1.5 | 6 | 37.6±0.5 | 5 |
| *R* 110 | smoked sheet | 32 | 19 | 11 | 35.2±0.3 | 14 | 35.1±1.2 | 5 |
| *R* 74 | smoked sheet | 13 | 13 | 8 | 28.8±1.0 | 7 | 28.4±0.7 | 4 |
| *R* 75 | smoked sheet | 11 | 18 | 8 | 29.7±0.2 | 3 | 30.0±0.7 | 4 |
| *R* 107 | crepe | 31 | 30 | 22 | 40.8±1.0 | 16 | 41.2±1.4 | 8 |
| *R* 113 | crepe | 12 | 20 | 15 | 33.8±0.8 | 18 | 31.0±0.5 | 3 |

*) $N$ is the number of samples examined.

If, on the other hand, such regions do exist, the above results would be compatible also with other crystal densities.

The author wishes to acknowledge the helpful discussions with Professor A. van Rossem, who kindly supplied valuable samples of raw rubber, and Professor H. B. Dorgelo, both of Delft University. He is indebted to Mr. de Wolff for the continuous interest in his work, to his assistant (Miss) M. van Roon, employee of the Rubber Foundation, who carried out so many experiments, and to the Rubber Foundation, which supported his work in this way. Thanks finally are due to the Delft University Fund for its support of this research.

## SUMMARY

In 1925 Katz discovered the crystallization of stretched rubber. In the following years several investigators tried to determine the structure of rubber crystallites.

The densities of the rubber crystallites calculated from the results of these investigations varied strongly. The results of $x$-ray and density measurements

on crude rubber carried out by the author can be made to correspond only when the latter are based on the unit cell of Bunn.

It is shown by experiment that, to measure the correct degree of crystallization, it is necessary to use monochromatic $x$-rays.

## REFERENCES

[1] Katz, *Naturwissenschaften* **13**, 411 (1925).
[2] Van Rossem and Lotichius, *Kautschuk* **5**, 2 (1929).
[3] Mark and von Susich, *Kolloid-Z.* **46**, 11 (1928).
[4] Lotmar and Meyer, *Sits. Ber. Akad. Wiss. Wien*, Abt. IIb, **145**, 721 (1936).
[5] Sauter, *Z. physik. Chem.* **36**, 405 (1937).
[6] Morss, *J. Am. Chem. Soc.* **60**, 237 (1938).
[7] Misch and van der Wijk, *J. Chem. Physics* **8**, 127 (1940).
[8] Bunn, *Proc. Royal Soc.* (London) **A180**, 40 (1942).
[9] Goppel, Thesis, Delft, 1946.
[10] In the $x$-Ray Department of the Delft Technical University, a direct intensity recording photometer devised by de Wolff (not yet published) is used.
[11] Simard and Warren, *J. Am. Chem. Soc.* **58**, 507 (1936); RUBBER CHEM. & TECHNOL. **9**, 417 (1936).
[12] Field, *J. Applied Physics* **12**, 23 (1941).
[13] Hermans, "Contribution to the Physics of Cellulose Fibers," Elsevier Publishing Co., 1946.

# IV. THE DEGREE OF CRYSTALLIZATION IN FROZEN RAW RUBBER AND STRETCHED VULCANIZED RUBBER

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## INTRODUCTION

Numerous researches on polymeric substances point to the importance of molecular motions as related to mechanical properties. The pronounced influence of temperature is illustrative of this. Molecular mobility in polymers depends on the interaction of the intrinsic mobility of the molecules and the intermolecular cohesion. This interaction is considerably different in amorphous and crystalline regions and, therefore, the degree of crystallization is closely connected with the properties of the polymer under consideration.

With regard to the crystallization in rubber, only little quantitative information exists. Field[1] was the first to carry out direct $x$-ray measurements to determine the proportion of crystallized rubber in stretched vulcanized natural-rubber compounds. According to this investigator a pure-gum vulcanizate may crystallize to the extent of 60–80 per cent at elongations of 500 per cent. These figures are very high when compared with estimates of earlier date, and it was decided to reinvestigate the matter[2]. From preliminary measurements it appeared that the $x$-ray technique had to be improved in such a way as to make possible various corrections to obtain a reasonable degree of accuracy. The $x$-ray method has already been described in some detail, but the results[3] were not corrected for the influence of the polychromatic radiation and Compton scattering. A method to account for these influences has been proposed by Arlman[4]. The authors believe that a combination of the $x$-ray technique already mentioned[5] and this improved interpretation leads to a rather accurate evaluation of the crystalline-amorphous ratio in natural rubber. The present paper deals with the results of the investigations, carried out on frozen crude rubber, as well as on stretched vulcanized rubber.

## THE AMOUNT OF CRYSTALLINE MATERIAL IN SAMPLES OF FROZEN RAW RUBBER

*Smoked sheet.*—Much work has already been done on the crystallization of raw unvulcanized rubber[6], and the degree of crystallinity has been estimated[7], but, as far as is known, only the present authors published direct measurements.

The problem can be attacked by $x$-ray analysis as described, and some measurements on frozen rubber were carried out. By courtesy of Professor Van Rossem we had at our disposal a collection of samples of smoked sheet, stored for different times, from a few years to about thirty years, and the degree of crystallization was determined. The accuracy of these determinations is somewhat smaller, compared with analogous measurements on stretched rubber, because if unstretched frozen rubber is investigated, the radiation scattered at relatively small angles must be used. To eliminate possible influences of crystallite orientation, $x$-ray diagrams were taken both with primary beam

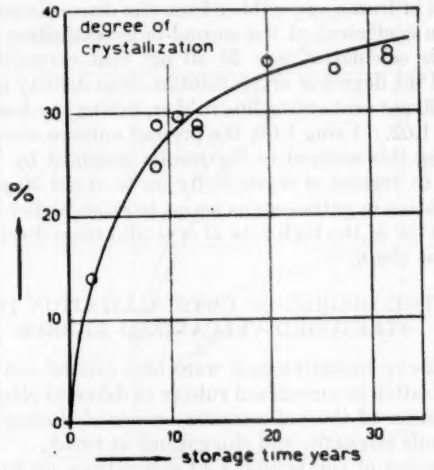


FIG. 1.—The degree of crystallization in samples of smoked sheet plotted as a function of the storage time.

parallel and perpendicular to the plane of the rubber sheet. No significant differences, however, could be observed. The results are represented in Figure 1. Though the $x$-ray measurements were carried out on different samples, we were strongly under the impression that each individual rubber actually crystallized during storage. It is not certain that, even after thirty years, equilibrium has been obtained. All samples have been stored at about 12° C, and the rate of crystallization at these temperatures is indeed very small[6].

*Crepe rubber.*—A close relationship between the storage time and the degree of crystallization could not be demonstrated for samples of crepe rubber, though these had been stored under the same conditions as the smoked sheet. In one sample of twenty-nine year old crepe, a considerable range of crystallinities was found from 30 to 48 per cent. The degree of crystallinity was in several cases considerably in excess of the maximum value, 35 per cent, found for smoked sheet. This may be explained by variations in the degree of molecular

orientation caused by the difference in manufacturing process, as this orientation is known to have a marked effect on the rate of crystallization[8].

*Rubbers of different botanical origin.*—Some samples of rubber other than Hevea brasiliensis were examined, *viz.*, hard fine Para, Landolphia Boké and Ficus elastica, as well as a sample of Tjipetir gutta-percha. The results are given in Table 1.

TABLE 1

| Hydrocarbon | Storage time (years) | Degree of crystallization (%) |
|---|---|---|
| Landolphia Boké | 28 | 29 |
| Ficus elastica | 23 | 32 |
| Hard fine Para | 27 | 33 |
| Tjipetir gutta | — | 55–60 |

The degree of crystallization in rubber generally is small, as was born out by experiments by Parks; he calculated the amount of crystalline rubber in unstretched samples of frozen raw rubber from the discontinuous variation of the volume expansion coefficient at the second-order transition point at −72° C. The result of this calculation was 20–30 per cent crystallinity. Smith and Saylor[9] estimated the degree of crystallization from density measurements, and arrived at about 30 per cent crystalline rubber, taking the density of the crystalline rubber to be 1.02. Using 1.00, the present authors arrive at about 40 per cent. In applying this method to the results obtained by Wood and Bekkedahl[6], one comes to degrees of crystallinity up to about 30 per cent.

The crystallization in gutta-percha seems to reach higher values, which may be expected in virtue of the high rate of crystallization displayed by this form of the polyisoprene chain.

## THE DEGREE OF CRYSTALLIZATION IN STRETCHED VULCANIZED RUBBER

Quantitative *x*-ray measurements were also carried out to determine the degree of crystallization in vulcanized rubber at different elongations. Table 2 gives the composition of the vulcanizates examined during the investigation, together with tensile strengths and elongations at break.

The crystallization of compound *A* at elongations up to 550 per cent was investigated, and it was shown that the degree of crystallization at this elongation amounts to about 35 per cent. The compounds *D*1 − *D*4 were chosen to investigate the influence of the curing time on the crystallization; they corre-

TABLE 2

| Compound | *A* | *D*1 | *D*2 | *D*3 | *D*4 | *F* | *G* |
|---|---|---|---|---|---|---|---|
| Crepe | — | — | — | — | — | 100 | — |
| Smoked sheet | 100 | 100 | 100 | 100 | 100 | — | 100 |
| Sulfur | 1.75 | 5 | 5 | 5 | 5 | — | 2 |
| Zinc oxide | 5 | 3 | 3 | 3 | 3 | 5 | 1 |
| Diphenylguanidine | 0.5 | 1 | 1 | 1 | 1 | — | — |
| Tetramethylthiuram disulfide | — | — | — | — | — | 3 | — |
| Mercaptobenzothiazole | 0.8 | — | — | — | — | — | 1 |
| Stearic acid | 1 | — | — | — | — | — | 1 |
| Aldo-alpha-naphthylamine | 1 | — | — | — | — | — | — |
| Vulcanization (min.) | 30 | 15 | 30 | 45 | 60 | 30 | 30 |
| Degrees (° C) | 142 | 142 | 142 | 142 | 142 | 135 | 141 |
| Tensile strength (kg./mm.²) | 28.8 | 26.6 | 27.3 | 22.1 | 18.9 | 21.3 | 19.6 |
| Elongation (%) | 717 | 810 | 744 | 638 | 646 | 761 | 968 |

spond to a series, also examined by Field[1]. Compound *F* is a heat-resisting mixture, which was used in some experiments to establish the effect of temperature on the degree of crystallization. Compound *G* corresponds to a vulcanizate used by Holt and McPherson[10] in the density measurements.

## THE DEGREE OF CRYSTALLIZATION IN RELATION TO THE VULCANIZATION PERIOD

The crystallization of the compounds *D*1 – *D*4 was determined as a function of the elongation, and the results of the measurements indicate an initial increase, followed by a decrease in the degree of crystallization if vulcanization is increased from 15 to 60 minutes. So far they agree with the results of Field, but a remarkable discrepancy exists with regard to the maximum degree of crystallization. The present results are represented in Figure 2.

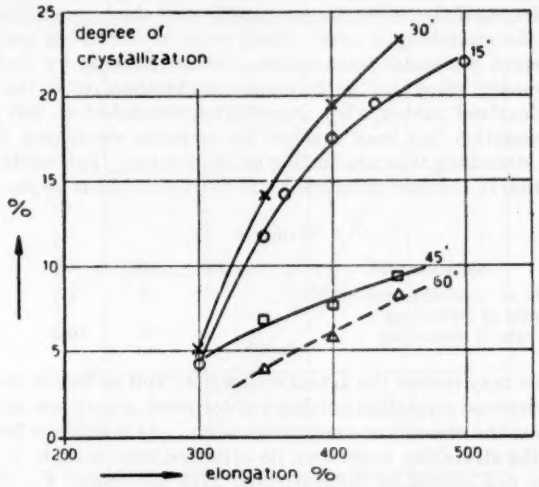


FIG. 2.—The amount of crystalline rubber as a function of the elongation and period of vulcanization (indicated on the curves) for compounds *D*1 to *D*4.

In Table 3 the degree of crystallization at an elongation of 400 per cent is compared with the moduli at 200 and 400 per cent.

In accordance with modern views[11], a moderate increase in the degree of cross-linking results in a higher degree of crystallinity and a higher tensile strength (compare Table 2). In overcured samples (45 and 60 minutes) the cross-linking becomes so important that crystallization is considerably decreased. That the increase in modulus with vulcanization is largely caused by cross-linking and not by crystallization is also indicated by the fact that the

TABLE 3

| Curing time (min.) | 15 | 30 | 45 | 60 |
|---|---|---|---|---|
| Modulus at 200% (kg. per sq. cm.) | 9 | 12 | 18 | 16 |
| Modulus at 400% (kg. per sq. cm.) | 20 | 32 | 46 | 46 |
| Degree of crystallization (20° C at 400% (%)) | 17.5 | 18.5 | 7 | 5 |

overcured compounds cannot endure prolonged elongation. This is probably caused by scission of chains or cross-links, followed by a slipping of the chains, the probability of which is enhanced by the absence of crystallization.

## THE CONDITIONS OF STRETCHING

In all series where crystallization was considered as a function of the elongation, stretching of the rubber was carried out in steps of 50 or 100 per cent, the rate of stretching being about 100 per cent per minute. The samples were left in the stretched condition during the *x*-ray exposure (exposure time 5 minutes) and subsequently stretched to the new elongation. This differs from Field's way of stretching, who used a falling-weight method.

According to Acken and coworkers[12], the time involved in building up the crystal lattice in stretched rubber may be of the order of 1 second. If the process of stretching involves a time $> 1$ second, the rubber can crystallize during elongation, whereas if the rubber is very rapidly stretched, crystallization mainly occurs when the stretching is over. Both ways of stretching may, therefore, result in different molecular orientations. Measurements by Holt and MacPherson[10], however, show that no difference can be observed in the density of a sample of vulcanized rubber when immediately stretched to 600 per cent, or when this elongation has been reached by stepwise stretching, the time involved in the stretching then amounting to 18 minutes. Estimating the degree of crystallization in the case mentioned, one arrives at about 25 per cent.

TABLE 4

| Elongation (%) | 200 | 300 | 400 | 500 |
|---|---|---|---|---|
| Degree of crystallization at 20° C | | | | |
| Low rate of stretching | 1.0 | 2 | 7.4 | 11.5 |
| High rate of stretching | — | 5 | 10.5 | 16.5 |

Plastic flow may reduce the actual elongation, and as flow is favored at low elongations where no crystallization has yet occurred, a very low rate of stretching may reduce the crystalline-amorphous ratio. As is evident from the work cited above, the stretching must then be extended over periods $> 18$ minutes.

This effect can indeed be demonstrated with compound *F*. One series of *x*-ray measurements was carried out on rapidly stretched samples, another on a sample which was stretched very slowly, the period of stretching involving some days. The differences in degree of crystallization in both cases are listed in Table 4.

The time in which the high rate stretching was completed amounted to 10–20 seconds. In view of the enormous differences in stretching rates and the comparatively small effect on the degree of crystallization, small variations in the standard stretching conditions are not likely to affect the results to any appreciable extent.

## CORRELATION BETWEEN X-RAY RESULTS AND DENSITY MEASUREMENTS

Accurate density measurements on stretched vulcanized rubber[10] show that crystallization is attended by a decrease in volume, and from this contraction the degree of crystallization can be calculated if the density of completely crystallized rubber is known. This density can be calculated from unit cell dimensions, obtained from *x*-ray data, but unfortunately several investigators

are not entirely agreed upon the $x$-ray density, and a small error in this density results in a considerable error in the degree of crystallization, which may be derived from:

$$K = \frac{v_a}{v_a - k_k}\left(1 - \frac{v}{v_a}\right),$$

where $v_a$ = specific volume of amorphous rubber
$v_k$ = specific volume of crystalline rubber
$v$ = specific volume of stretched, partially crystalline rubber.

Substituting for $v_a$ the value 1.094 of Wood and Bekkedahl[6] and for $v_k$ the value 1.00 according to the $x$-ray analysis by Bunn[13], the above formula may be applied to the results of Holt and McPherson[10]. Relatively low degrees of crystallization are thus found.

$x$-Ray measurements were carried out in the present work on a compound of the composition used by Holt and McPherson in their density measurements.

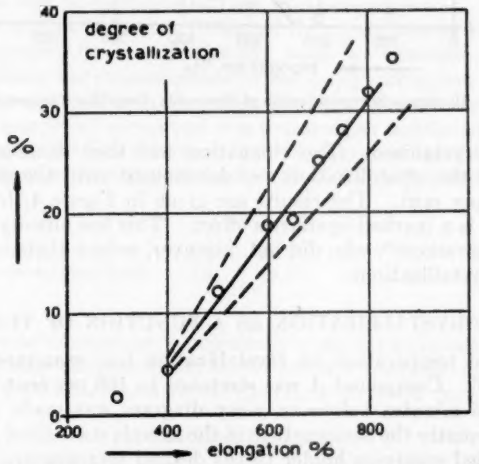


FIG. 3.—The degree of crystallization in a pure-gum compound. Plots are $x$-ray measurements; the full line is obtained from density data from literature. The dotted lines indicate the effect of an error of 0.02 in the density of amorphous or crystalline rubber (Compound $G$).

This compound is indicated by $G$ in Table 1 and, indeed, very low degrees of crystallization were found. The results are represented in Figure 3, where the crystallization values according to the density measurements are indicated by the solid line. The dotted lines represent variations of 0.02, either in $v_a$ or $v_k$. The agreement is satisfactory and leaves little doubt as to the order of magnitude of the degree of crystallization.

## HYSTERESIS IN CRYSTALLIZATION

Hysteresis in crystallization with regard to decreasing elongation was investigated for compound $F$. A sample of this compound was stretched stepwise from 0 to 600 per cent, and the degree of crystallization was determined for every 50 per cent increase in elongation. At 600 per cent, about 19.5 per cent

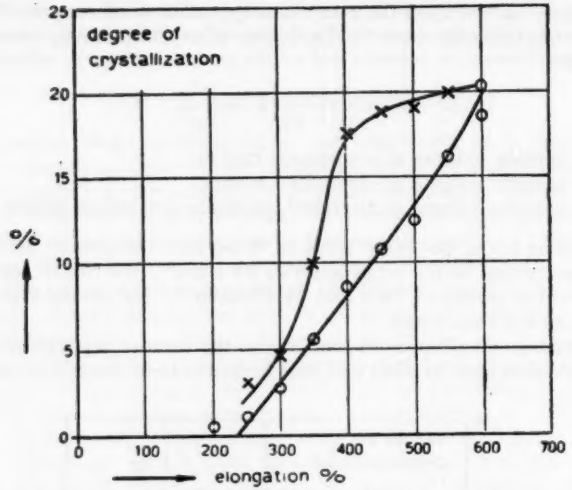


FIG. 4.—Hysteresis in crystallization at decreasing elongation (Compound F.)

of the rubber crystallized. The elongation was then decreased in steps of 50 per cent and the crystallization was determined until the sample was contracted to 250 per cent. The results are given in Figure 4, from which it is clear that there is a marked hysteresis effect. This has already been observed by Clark and coworkers[14], who did not, however, reduce their $x$-ray intensities to degrees of crystallization.

## DEGREE OF CRYSTALLIZATION AS A FUNCTION OF TEMPERATURE

The effect of temperature on crystallization was examined for the compounds *A* and *F*. Compound *A* was stretched to 460 per cent and left in this condition for 45 minutes before an $x$-ray diagram was made (exposure time 0.5 *h*). Subsequently the temperature of the sample was raised by means of an electrically heated specimen holder to the desired temperature, and the $x$-ray diagram was made after the sample had been left for 45 minutes at this higher temperature, etc. The results are given in Table 5, together with two measurements on a sample stretched to an elongation of 40 per cent.

In view of the results obtained by Wildschut[15], no equilibrium with respect crystallization was reached under the conditions of these experiments because of the considerable delay in melting displayed by the crystallites in stretched rubber.

Similar experiments were carried out with compound *F*. A sample of this compound was first stretched to 500 per cent, then heated for 1 hour at 100° C.

TABLE 5

| Temperature (° C) | 17 | 30 | 40 | 50 | 60 | 70 | 80 |
|---|---|---|---|---|---|---|---|
| Degree of crystallization at elongation of 460% | 24.3 | 19.9 | 19.2 | 17.9 | 15.4 | — | 13.1 |
| 460% | 25.1 | — | — | — | 15.6 | — | — |
| 400% | 14.7 | — | — | — | — | 6.0 | — |

Then an $x$-ray diagram was made, the rubber being kept at 100° C; subsequently the temperature was lowered to 90° C. After 1 hour another $x$-ray diagram was taken, etc. The lowest temperature reached in this series amounted to 13° C, and finally the rubber was gradually heated to 110° C, $x$-ray diagrams being taken at the same intervals. The results are tabulated in Table 6.

TABLE 6

| Temperature (° C) | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|
| Degree of crystallization at 500% elongation | | | | | | | | | | |
| → | — | 4.1 | 3.8 | 5.9 | 6.5 | 7.5 | 7.6 | 8.6 | 11.2 | 14.7 |
| ← | 2.9 | 5.9 | 7 | 9.0 | 8.4 | — | 10.3 | 11.7 | 12.0 | — |

It will be noted that the degree of crystallization in compound $F$ (Table 6) is small when compared with compound $A$ (Table 5). A possible explanation of this difference will be discussed in Part V of this series[16].

As already described[17], the orientation of the crystallites in stretched rubber may be characterized by a half-intensity angle $\varphi$, obtained from intensity measurements along the circumference of the $x$-ray diffraction spots. It was observed that the orientation of the crystallites varies markedly with the temperature. If a sample of compound $F$ is examined at increasing temperatures, the degree of crystallization decreases and the degree of orientation of the remaining crystallites increases, as is evident from Table 7, where the values of

TABLE 7

| Temperature (° C) | 18 | 30 | 40 | 70 | 80 | 100 |
|---|---|---|---|---|---|---|
| Crystallite orientation $180/\varphi$ | 13 | 15.5 | 16 | 18 | 20.5 | 23 |

$180/\varphi$ are listed.

As the degree of orientation is practically constant at increasing tension or elongation[17], the only explanation of these results is that the crystallites which are poorly oriented with respect to the direction of stretch melt first.

## RECRYSTALLIZATION

Various investigators have already stressed the importance of crystallization for the mechanical properties of rubber. The effect of crystallization is described as cross-linking or filler action[18]. On the other hand there is experimental evidence that the elastic tension in stretched rubber decreases as a result of crystallization[19]. This paradox has been solved by Flory[20], who showed that it is actually caused by two different ways of crystallization. If crystallization occurs in a highly stretched rubber, the elastic tension is reduced, as is evident from experiment[19] and theory[20]. It will be shown in Part V that the agreement between both is not only qualitative, but that Flory's theory may explain quantitatively the dependence of tension on temperature, as actually observed. If, on the other hand, crystallites are formed during the stretching process, no equilibrium state is reached according to Flory; the crystallites act as cross-linkages or fillers which greatly affect the increase of tension with elongation.

It has been shown in the present work that the orientation of the crystallites is related to the melting temperature. If a sample of stretched vulcanized

rubber is heated, the less oriented crystallites disappear first. It was found, on cooling, that the degree of crystallization again increases, but that the orientation of the crystallites is markedly better than in the case of the original material. A sample of compound *A*, stretched to an elongation of 500 per cent, displayed a crystallite orientation corresponding to a $180/\varphi$ value of 18. After heating for 4 hours at 70° C and cooling the rubber to 20° C, this value had increased to 22. The degree of crystallization was also determined, and was found to have increased from 28 to 31 as a result of the heat treatment. A recrystallization seems to have taken place, during which "filler-type" crystallites have at least partially disappeared and "equilibrium-type" crystallites have been formed. Very schematically this might be represented by Figure 5.

FIG. 5.—Schematic representation of the recrystallization due to a heat treatment at 70° C. *a*. Crystallization upon stretching, 20° C. *b*. Part of the crystallites melt at heating to 70° C. *c*. On cooling to 20° C a higher degree of orientation is observed.

Emphasis must be laid on the small differences between the degrees of equilibrium and normally obtained crystallizations. It has been shown for two different compounds (*A* and *F*), crystallizing to different degrees, that the degree of crystallization obtained by cooling of heated stretched rubber and by normal stretching are about the same, as is evident from Table 8.

TABLE 8

| Compound | Degree of crystallization (%) | |
|---|---|---|
| | In normal stretching | By cooling a heated stretched specimen |
| *A* (500%) | 28 | 31 |
| *F* (500%) | 16.3 | 14.7 |

## CONCLUSIONS

By means of an *x*-ray method the degree of crystallization in unstretched, raw rubber and in stretched vulcanized rubber was determined. The highest degree of crystallization was found to occur in a 29 year-old sample of crepe rubber, and amounted to 48 per cent. Generally, the degree of crystallization was considerably lower. Vulcanized pure-gum compounds at an elongation of 500 per cent were found to have crystallinities of 15–30 per cent, depending on the composition of the vulcanizates.

The crystallization has been investigated as a function of curing time, elongation, and temperature; the results indicate recrystallization at higher temperatures.

ACKNOWLEDGMENT

The authors wish to acknowledge the helpful discussions with Professor A. Van Rossem, who also kindly supplied valuable samples of raw and vulcanized rubber, and with Professor H. B. Dorgelo, both of Delft University. Their continued interest is very much appreciated.

Thanks are finally due to the Delft University Fund for its support of this research, and to the directors of the Rubber Foundation for their permission to publish the results.

SUMMARY

An improved $x$-ray technique has been worked out to determine the degree of crystallinity in natural rubber. Inaccuracies which sometimes occur in quantitative $x$-ray measurements were eliminated, and it has been shown that the amount of crystalline rubber, both in frozen samples of raw rubber and in stretched vulcanized rubber, could be determined fairly accurately. More experiments were carried out and the results are described. These results, which confirm the current views on the problem of crystallization, point to relatively low degress of crystallization, even in highly stretched rubber, and they agree with some other experimental evidence and with a recent theoretical investigation[20].

REFERENCES

[1] Field, *J. Applied Physics* **12**, 23 (1941).
[2] The investigation formed part of a program of rubber research, carried out in Holland during the War, and part of which was published as a thesis (Goppel, Thesis, Delft Univ., "Quantitatieve röntgenografische onderzoekingen aan Rubber," 1946.
[3] Goppel, *Proc. Rubber Tech. Conf. London*, 1948, p. 164.
[4] Arlman, *Applied Sci. Research* **A1**, 347 (1948); this issue of RUBBER CHEM. & TECHNOL.
[5] Goppel, *Applied Sci. Research* **A1**, 3 (1947); RUBBER CHEM. & TECHNOL. **21**, 773, 783 (1948).
[6] Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946).
[7] Parks, *J. Chem. Physics* **4**, 459 (1936).
[8] Goppel and Van Rossem, *Physica* **9**, 213 (1942).
[9] Smith and Saylor, *Bur. Standards J. Research* **21**, 257 (1938).
[10] Holt and McPherson, *Ind. Eng. Chem.* **17**, 657 (1936).
[11] Field, *J. Applied Physics* **12**, 23 (1941); Gee, *J. Polymer Sci.* **2**, 451 (1947).
[12] Acken, Singer, and Davey, *Ind. Eng. Chem.* **24**, 54 (1932).
[13] Bunn, *Proc. Royal Soc.* (London) **A180**, 40 (1942).
[14] Clark, Kabler, Blaker, and Ball, *Ind. Eng. Chem.* **32**, 1474 (1940).
[15] Wildschut, *J. Applied Physics* **17**, 51 (1946); "Technological and Physical Investigations of Natural and Synthetic Rubbers," 1946.
[16] This issue of RUBBER CHEM. & TECHNOL.
[17] Goppel, Thesis, Delft Univ., "Quantitatieve röntgenografische onderzoekingen aan Rubber," 1946.
[18] Field, *J. Applied Physics* **12**, 23 (1941); Guth, James, and Mark, "The kinetic theory of rubber elasticity," in Advances in Colloid Science, II (1946); Gee, *J. Polymer Sci.* **2**, 451 (1947).
[19] Meyer and Ferri, *Helvetica Chim. Acta* **18**, 570 (1935); Wildschut, *J. Applied Physics* **17**, 51 (1946); "Technological and Physical Investigations of Natural and Synthetic Rubbers," 1946.
[20] Flory, *J. Chem. Physics* **15**, 397 (1947).

# V. A DISCUSSION OF THE X-RAY RESULTS ON NATURAL RUBBER IN CONNECTION WITH THE WORK OF FLORY, GEE AND WILDSCHUT

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## INTRODUCTION

The experimental results presented in Part IV[1] of this series concerning the degree of crystallinity in stretched vulcanized rubber generally support the modern views on the matter; the puzzling disagreement with the results ob-

tained by Field[2] and with those obtained by Lukin and Kasatochkin[3] remains, however, unexplained.

The relatively low values for the degree of crystallization found by $x$-ray measurements have been shown to agree with density measurements on raw and vulcanized rubber, and there is also an indication that they correspond to results of optical measurements. Treloar[4] estimates, from birefringence measurements, that the degree of crystallization at 21° C in vulcanized rubber at an elongation of 525 per cent amounts to 39 per cent of that at an elongation of 700 per cent at 0° C.

## THE COMBINATION OF THERMODYNAMICAL AND X-RAY MEASUREMENTS

Wildschut[5] also calculates the degree of crystallization, assuming that the decrease in tension on cooling is a linear function of the degree of crystallization. The results thus obtained on compound $A$[6] are in remarkable agreement with the $x$-ray measurements, as is evident from Figure 1.

The amount of crystallization in polymers has been derived by Flory[8] in a recent theoretical treatise as a function of temperature and elongation. He also calculated the decrease in tension on crystallization as a function of the degree of crystallization. According to Flory, at a temperature below the

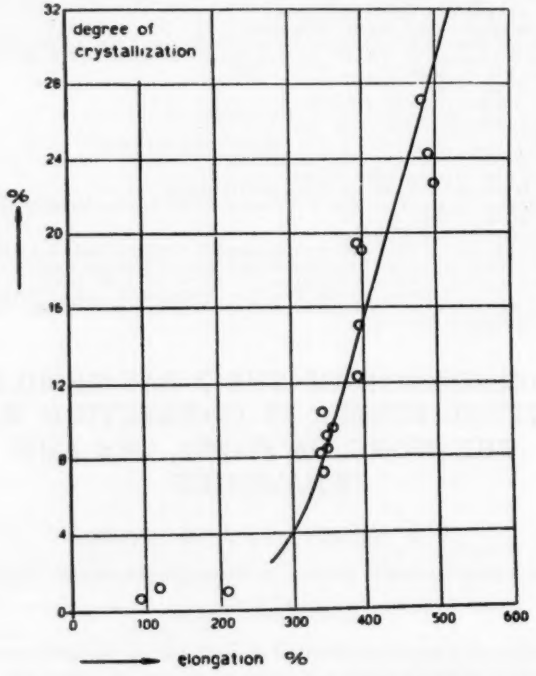


FIG. 1.—The degree of crystallization in compound $A$ as a function of the elongation. Plots refer to measurements of Wildschut. The drawn curve indicates $x$-ray results.

incipient crystallization point:

$$\frac{f_0 - f_K}{f} = \frac{K}{1 - K}\left[\frac{1}{\alpha}\sqrt{\frac{6n}{\pi}} - 1\right] \tag{1}$$

where

$f_0$ = tension which would be observed without crystallization
$f_K$ = actual tension
$\alpha$ = % elongation/100 + 1
$K$ = theoretical degree of crystallization
$n$ = number of chain segments between cross-linkages.

If the equilibrium degree of crystallization is determined by means of $x$-ray, density or optical measurements, the above formula permits a ready calculation of $n$.

It has already been indicated in Part IV of this series[7] that the degree of crystallization from the $x$-ray work is not likely to be very different from the equilibrium degree.

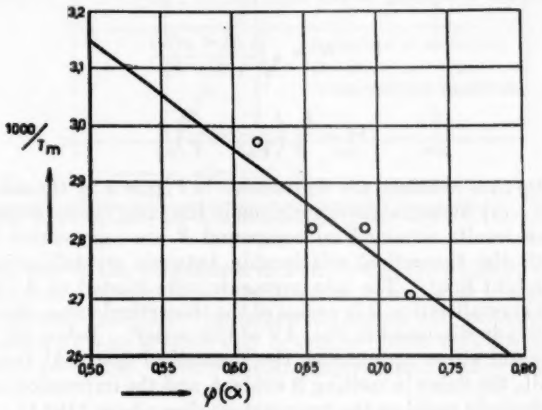


FIG. 2.—Relation between incipient crystallization temperature ($T_m$) and $\varphi(\alpha)$.

The degree of crystallization according to Wildschut $K'$ was calculated from:

$$K' = \frac{f_0 - f_K}{f_0} \tag{2}$$

From Figure 1 it is concluded that $K = K'$ for compound $A$ and thus:

$$\frac{1}{\alpha}\sqrt{\frac{6n}{\pi}} - 1 \cong 1 - K \tag{3}$$

which holds, with the observed values for $K$ as a function of $\alpha$, fairly well in the region of 400–600 per cent elongation if $n$ = 45 to 65.

Other compounds with different degrees of cross-linking may give important differences between $K$ and $K'$. Compound $F$, which has been investigated by Wildschut[6], shows $f_0$- and $f_K$-values which result in a value of $K'$ much in excess of the degree of crystallization obtained from $x$-ray data.

The value of $n$, for which there is good agreement between the experimental results of Wildschut and $x$-ray data, can be calculated, using Formula (1), and results in a value of 115 for the number of chain segments between cross-linkages.

According to Flory's theory,[8] there must be a linear relationship between $(T_m^\epsilon)^{-1}$, $T_m^\epsilon$, since the incipient crystallization temperature at an elongation $\epsilon$, and $\varphi(\alpha)$, is a function of the elongation, which can be easily calculated as soon as $n$ has been evaluated. Taking $n = 115$ and using incipient crystallization temperatures as determined by Wildschut, Figure 2 is obtained from which, according to the relation:

$$\varphi(\alpha) = \frac{h_f}{R}\left(\frac{1}{T_m^0} - \frac{1}{T_m^\epsilon}\right)$$

derived by Flory[8], $h_f/R$ and $T_m^0$ can be calculated.

The incipient crystallization temperature for the unstretched rubber turns out to be 243° K; for $h_f$, the heat of fusion per mole segment of the molecule chains, the value 1030 calories is obtained.

With these values the degree of crystallinity as a function of the elongation can be calculated according to the equation of Flory:

$$1 - K = \sqrt{\frac{1.5 - \varphi(\alpha)}{1.5 - \Theta}} \tag{4}$$

with:

$$\Theta = \frac{h_f}{R}\left(\frac{1}{T_m^0} - \frac{1}{T}\right)$$

and the values thus obtained are represented in Figure 3 by the solid line. The results of the $x$-ray measurements are given in the same figure by means of plots.

The $x$-ray results obtained on compound $F$ are represented in Figure 4, together with the theoretical relationship between crystallization and temperature (straight line). The measurements were started at $A$ (100° C), and the degree of crystallization is in excess of the theoretical value, due to the delay in melting already discussed in Part IV of this series[7]. Below 40° C, however, the experimental curve approaches the theoretical one. At increasing temperature again, the delay in melting is evident, and the impression is gained that melting is relatively rapid as the temperature rises above 110° C. Crystallization at 20° C, found by interpolation, has also been inserted in Figure 3, because it corresponds better to equilibrium when compared with the other experimental plots of Figure 3.

Finally the theoretical values of $n$, $T_m^0$, $h_f$ and $K$ are substituted in Formula (1), derived by Flory for the elastic tension as a function of the temperature. The theoretical relationship thus obtained closely corresponds to the actual measurements made by Wildschut, as can be concluded from Figure 5.

According to Gee[9], the degree of cross-linking may be deduced from swelling measurements and there is a close correlation between modulus and $M_c$, the molecular weight between the cross-linkages. From the figures given by Gee and the moduli found for the compounds in question, the $M_c$-values may be estimated. They amount to 5400 and 9600 for the compounds $A$ and $F$, respectively. This marked difference corresponds to the difference in $n$ values, which are 55 and 115, respectively.

The weight of one chain segment $M_c/n$ thus obtained is about 90, that is, somewhat higher than the weight of the repeating isoprene unit. Now that the value of $n$ is known, it is possible to verify the value of $h_f$, the heat of fusion per

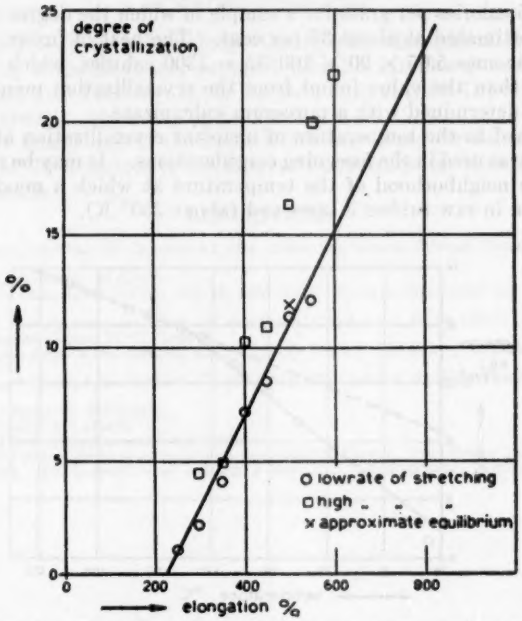


FIG. 3.—Degree of crystallization as a function of the elongation (compound *F*). Plots refer to *x*-ray measurements; solid curve represents the theoretical relation (Flory), with $n = 115$, $h/R = 520$, $T_m^0 = 243°$ K.

mole segment, one of the parameters in Flory's theory, which in the foregoing considerations was assumed to be 1030 calories. This value was obtained from the relation between incipient crystallization points and elongation.

A publication by Van Rossem and Lotichius[10] deals with the heat of fusion of crystallized raw rubber. From swelling measurements they found a heat of

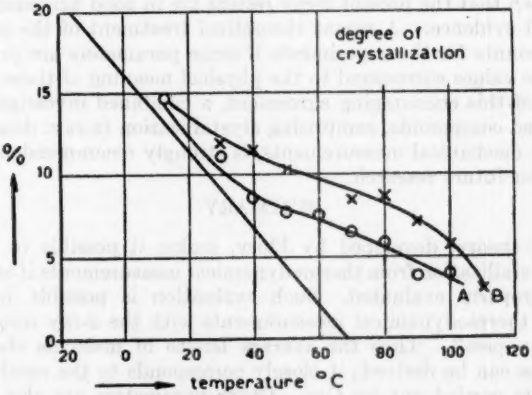


FIG. 4.—Degree of crystallization as a function of temperature (Compound *F*). Plots represent *x*-ray results; the linear relationship is demanded by Flory's theory.

fusion of 5.05 calories per gram for a sample in which the degree of crystallization can be estimated at about 35 per cent. The heat of fusion per mole segment thus becomes $5.05 \times 90 \times 100/35 = 1300$ calories, which is thus somewhat higher than the value found from the crystallization point—elongation relationship, determined with a pure-gum vulcanizate.

With regard to the temperature of incipient crystallization at zero elongation, 243° K was used in the foregoing considerations. It may be remarked that this is in the neighborhood of the temperature at which a maximum rate of crystallization in raw rubber is observed (about 250° K).

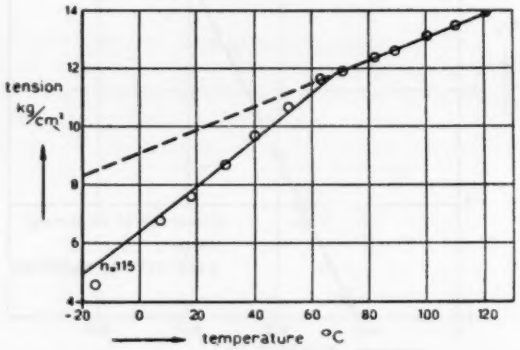


FIG. 5.—Decrease in elastic tension at decreasing temperature. Plots represent experimental results obtained by Wilkschut; the solid curve corresponds to theory (Compound *F*, 500 per cent elongation).

Summarizing, it can be said that the evaluation of different parameters, involved in Flory's theory, not only satisfactorily accounts for the *x*-ray results, but also is in reasonable agreement with what might have been expected from independent measurements.

## CONCLUSIONS

It is shown that the present *x*-ray results are in good agreement with other experimental evidence. A recent theoretical treatment of the problem satisfactorily accounts for the experiments if some parameters are properly evaluated. These values correspond to the physical meaning of these quantities.

In view of this encouraging agreement, a combined investigation on a set of well defined compounds, comprising crystallization (*x*-ray, density, optical), swelling and mechanical measurements, is strongly recommended as a promising outline for future research.

## SUMMARY

A recent theory, developed by Flory, makes it possible to calculate the degree of crystallization from thermodynamical measurements if certain parameters are properly evaluated. Such evaluation is possible by combining Wildschut's thermodynamical measurements with the *x*-ray results presented in previous papers[11]. Thus the average length of molecule chains between cross-linkages can be derived; it closely corresponds to the results of swelling measurements carried out by Gee. Other parameters are also evaluated in agreement with their physical meaning.

## ACKNOWLEDGMENT

The authors wish to acknowledge the helpful discussions with Professor A. Van Rossem, who also kindly supplied valuable samples of raw and vulcanized rubber, and with Professor H. B. Dorgelo, both of Delft University. Their continued interest is very much appreciated.

Thanks are finally due to the Delft University Fund for its support of this research and to the directors of the Rubber Foundation for their permission to publish the results.

## REFERENCES

[1] Goppel and Arlman, *Applied Sci. Research* **A1**, 462 (1948); this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[2] Field, *J. Applied Physics* **12**, 23 (1941).
[3] Lukin and Kasatochkin, *Zhur. Tekhnic. Fiz.* **16**, 1383 (1946); RUBBER CHEMISTRY AND TECHNOLOGY **21**, 621 (1948).
[4] Treloar, L. R. G., private communication; see also *Trans. Faraday Soc.* **37**, 84 (1941).
[5] Wildschut, *J. Applied Physics* **17**, 51 (1946).
[6] Arlman and Goppel, *Applied Sci. Research*, **A1**, 462 (1948); Table 2; this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[7] Arlman and Goppel, *Applied Sci. Research* **A1**, 462 (1948); This issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[8] Flory, *J. Chem. Physics* **15**, 397 (1947).
[9] Gee, *J. Polymer Sci.* **2**, 451 (1947).
[10] van Rossem and Lotichius, *Kautschuk* **5**, 2 (1929).
[11] The results of this procedure have already been described (*cf.* Goppel, *Proc. Rubber Tech. Conf. London*, 1948, p. 164). The present paper contains a more elaborate treatment, based on more accurate values.

# THE REACTION OF SULFUR AND SULFUR COMPOUNDS WITH OLEFINIC SUBSTANCES VI. FACTORS INFLUENCING CYCLIC SULFIDE FORMATION IN THE REACTION OF SULFUR WITH POLYISOPRENES *

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The reaction of sulfur with polyisoprenes[1] yields di-tertiary cyclic sulfides[2] in addition to intermolecularly linked polysulfides, in which an average of four sulfur atoms has become interposed between a pair of polyisoprene molecules, with an overall loss of one double bond. Although the structure of these polysulfides has not yet been ascertained with certainty, there is every reason to believe that they are alkyl-alkenyl in type, by analogy with the general mode of reaction of sulfur with olefins[1].

Prolongation of the time of reaction of sulfur with olefins always results in the formation of some nonvolatile material of reduced hydrogen-to-carbon ratio[3] as a result of the reaction of primarily-formed polysulfides with centers of olefinic unsaturation present, either in the polysulfides themselves or in the excess of olefin which is usually maintained in these reactions[4]. The loss of unsaturation resulting from these secondary reactions has been effectively demonstrated[5].

Reference has also been made[4] to the ready formation of cyclic sulfides when bis-dihydromyrcene polysulfide is heated with dihydromyrcene, and it is now established that the proportion of cyclic sulfide to intermolecular polysulfide (*i.e.*, cross-linked material) in the mixture obtained by the reaction of sulfur with dihydromyrcene varies with the reaction time. When these reactants are heated at 141° for longer than three hours, only a comparatively small increase in the yield of intermolecular polysulfides results, in spite of the fact that much free sulfur is still present, and this suggests that existing cross-linkages are being converted to cyclic sulfide at a rate comparable with the formation of fresh cross-linkages (Table I). As the reaction proceeds further, and the proportion of free sulfur present diminishes, the former rate may even exceed the latter. Even in quite short reaction periods, cyclic sulfide is not entirely absent, indicating that some of the cyclic sulfide originates in the sulfur-polyisoprene reaction itself.

It follows from the foregoing that any substance which increases the rate of reaction of sulfur with rubber will, by enabling a given amount of sulfur to enter into reaction in a shorter time, give a greater proportion of cross-linked polysulfide relative to cyclic sulfide, and so increase the efficiency of the sulfur as a cross-linking reagent—always provided that the auxiliary substance does not

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also increase the rate of reaction of the polysulfide with the olefin. The so-called accelerators developed empirically by the rubber industry greatly facilitate the incorporation of sulfur into rubber, and recent work has shown that these substances similarly increase the rate of reaction of sulfur with olefins generally[6]. Such auxiliary substances could conceivably influence the reaction of sulfur with polyisoprenes in any of three ways: (1) by altering the relative proportions of cyclic sulfide and polysulfide, either in the manner just indicated, or by promoting a cross-linking rather than a cyclizing reaction of the sulfur[2], (2) by influencing the average number of sulfur atoms in the cross-linkages, or, (3) by influencing the unsaturation pattern adjacent to the sulfur linkage. Clearly, both (1) and (2) would affect the cross-linking efficiency of the sulfur, while the effect of (3) would be more apparent in the ultimate properties of the product, *e.g.*, its oxidizability or its thermal stability. The complexity of the cross-linked sulfuration products of polyisoprenes renders these materials rather unsuitable for studying the effects of (2) and (3) and a study of simple monoölefins, to be reported in a subsequent paper, is more informative. There is, however, already available some indication of positive effects which accelerators have on both the nature of the cross-linkage and its associated unsaturation pattern.

TABLE I

INFLUENCE OF REACTION TIME ON CROSS-LINKING EFFICIENCY IN DIHYDROMYRCENE AT 141° C
(10 parts sulfur per 100 hydrocarbon)

| Expt. no. | Time of heating (hours) | Combined sulfur %* | Weight ratio† | Sulfur ratio‡ |
|---|---|---|---|---|
| 1 | 1.5 | 1.4 | 5.6 | 10 |
| 2 | 3 | 3.0 | 4.4 | 8 |
| 3 | 6 | 3.8 | 2.9 | 5 |

* Weight of sulfur which has reacted with 100 grams of hydrocarbon.
† Ratio of weight of polysulfide to weight of cyclic sulfide.
‡ Ratio of sulfur in polysulfide linkages to sulfur in intramolecular cyclic linkages.

Armstrong, Little and Doak[6] observed an increase in the yield of monosulfides and a decrease in that of polysulfides when mercaptobenzothiazole was used to accelerate the reaction of sulfur with 2-methylbutene-2. Significant differences in unsaturation value and in the nature of the reaction of methyliodide with rubbers vulcanized in the presence of various accelerators have also been reported[7].

The results now presented in Table II clearly reveal that some common accelerators exert a pronounced effect on the cross-linking efficiency of sulfur with the diisoprene, dihydromyrcene.

The behavior of mercaptobenzothiazole and benzothiazyl disulfide at first appeared to be anomalous (Experiments 5–10), but it was later observed that traces of nitrogenous bases of a type rather similar to the decomposition products of some of the naturally occurring nitrogenous components of raw rubber[8] markedly influence (in an unknown manner) the mode of action of these particular accelerators. This behavior provides a probable explanation of the difficulties experienced by McColm and Haefele[9] and by Martin [10] in obtaining satisfactory vulcanization of highly purified rubber hydrocarbon when mercaptobenzothiazole was used as accelerator.

A further peculiarity of mercaptobenzothiazole in rubber vulcanization is that it requires the presence of a trace of water before it can exert its maximum

TABLE II

INFLUENCE OF ACCELERATORS ON CROSS-LINKING EFFICIENCY IN THE SULFUR-DIHYDROMYRCENE REACTION

(10 parts sulfur per 100 hydrocarbon)

| Expt. no. | Accelerator | Auxiliary substances * | Time (min.) | Temp. (° C) | Combined sulfur (%) | Weight ratio | Sulfur ratio | Transformation products of accelerators |
|---|---|---|---|---|---|---|---|---|
| 5 | MBT | — | 30 | 141 | 1.7 | 1.6 | 3 | |
| 6 | MBT | 1 | 30 | 141 | 2.8 | 2.2 | 4 | |
| 7 | MBT | 1, 3 | 30 | 141 | 1.6 | 1.8 | 3 | |
| 9 | MBT | 1, 2 | 30 | 141 | 3.0 | 5.0 | 9 | MBTS and zinc salt of MBT |
| 10 | MBT | 2 | 30 | 141 | 4.2 | 2.5 | 4.5 | |
| 14 | MBT | 1, 2, 4 | 30 | 141 | 2.3 | 7 | 12 | |
| 12 | MBTS | 1, 2 | 30 | 141 | 0.3 | — | — | Reaction insignificant |
| 15 | MBTS | 1, 2, 4 | 30 | 141 | 2.4 | 9.3 | 15 | |
| 16 | DPG | 1, 2 | 45 | 141 | 2.0 | >40 | >80 | Complex polysulfide |
| 18 | ZDC | — | 15 | 141 | 2.4 | 4.9 | 7.5 | |
| 19 | ZDC | — | 60 | 100 | 2.0 | 6 | 10 | |
| 20 | TMT | 1, 2 | 20 | 141 | 2.2 | 5.5 | 13 | Zinc dimethyldithiocarbamate |

* Auxiliary substances (see experimental section) as follows: 1, zinc oxide; 2, zinc propionate; 3, stearic acid; 4, tetramethylammonium stearate.

effect in increasing the cross-linking efficiency of sulfur (Table III). This effect is reflected in the proportion of zinc sulfide formed from the zinc oxide always used in conjunction with this accelerator; it has been suggested[11] that the zinc sulfide formed provides a measure of the degree of cross-linking.

Nitrogenous accelerators of the diphenylguanidine type appear to suppress the formation of cyclic sulfide altogether. It is perhaps significant that these substances also catalyze the conversion of thiols (which have been postulated as intermediates in cyclic sulfide formation[2]) to polysulfides in the presence of sulfur[13] and are capable of bringing rapidly into solution the insoluble modification of sulfur present in flowers of sulfur[14].

An example has been included in this paper of an accelerator, tetramethylthiuram disulfide, which is capable of effecting cross-linking in the absence of elementary sulfur, since it has been obscure whether this substance functions by promoting carbon-carbon cross-linkages[15] or by liberating a reactive form of sulfur[16]. It has long been known that tetramethylthiuram disulfide decomposes at temperatures above 100° C, giving tetramethylthiourea, carbon disulfide and sulfur[17], and the rate of this decomposition (see below) is appreciably increased in the presence of rubber hydrocarbon. In the presence of zinc oxide, normally used in admixture with tetramethylthiuram disulfide in the

TABLE III

INFLUENCE OF MOISTURE ON MERCAPTOBENZOTHIAZOLE ACCELERATED VULCANIZATION

| Conditioning of sample | Cure at 141° C (min.) | Combined sulfur % | Sulfur as ZnS % | Swelling index* (Qm.) |
|---|---|---|---|---|
| Dry | 20 | 0.75 | .002 | 6.2 |
| Wet | 20 | 1.7 | .041 | 4.5 |
| Dry | 45 | 1.7 | .024 | 5.0 |
| Wet | 45 | 2.05 | .075 | 4.5 |
| Dry | 90 | 2.05 | .062 | 4.8 |
| Wet | 90 | 2.6 | .141 | 4.1 |

* For the significance of Qm. as a quantitative indication of the degree of cross-linkage (see Gee[12]).

so-called sulfurless vulcanization of rubber, the formation of zinc dimethyldithiocarbamate has also been observed[18].

In its reaction with dihydromyrcene in the presence of zinc oxide, tetramethylthiuram disulfide is now shown to give a reaction product easily separable into two distinct fractions. One of these (not necessarily homogeneous) contains only carbon, hydrogen and sulfur, the latter in proportion too great for a monosulfide and rather too low for a disulfide; there is also some H/C deficiency. The other fraction contains both nitrogen and sulfur, and its composition indicates combination of a $Me_2N.C.S$-fragment with a dihydromyrcene molecule. The formation of these reaction products is in conformity with the usual finding of 0.4 to 0.5 per cent of combined sulfur in rubbers vulcanized with tetramethylthiuram disulfide. Both tetramethylthiuram monosulfide and zinc dimethyldithiocarbamate are separable from the dihydromyrcene reaction products; both have been isolated from the corresponding rubber-thiuram vulcanizates[19]. Tetramethylthiuram disulfide is thus seen to function as a sulfur-liberating agent, giving both mono- and disulfide cross-linkages; cyclic

TABLE IV

| Experiment no. | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|
| Dihydromyrcene | 50 | 50 | 50 | 50 | 50 | 50 | 100 | 50 | 50 |
| Sulfur | 5 | 5 | 5 | 5 | 5 | 5 | 3 | 5 | 5 |
| Zinc oxide | — | 2.5 | 2.5 | 2.5 | 2.5 | — | 5 | 2.5 | 2.5 |
| Stearic acid | — | — | 0.5 | 0.5 | — | — | — | — | — |
| Zinc propionate | — | — | — | — | 0.25 | 0.25 | 0.5 | 0.25 | 0.25 |
| Mercaptobenzothiazole | 1 | 1 | 1 | 0.25 | 1 | 1 | 1 | — | 1 |
| Tetramethylammonium stearte | — | — | — | — | — | — | — | 0.5 | 0.5 |
| Yield cyclic sulfide (g.) | 1.25 | 1.65 | 1.7 | 1.07 | 0.9 | 2.1 | 0.2 | 0.2 | 0.46 |
| Yield polysulfide (g.) | 2.0 | 3.7 | 3.5* | 1.9 | 4.4 | 5.2 | 1.0 | 1.3 | 3.25 |

* Found: C, 59.0; H, 8.7; S, 32.3.
0.33 g. of zinc sulfide was formed in Expt. 9.

sulfide formation is negligible. Carbon-carbon cross-linking is not entirely excluded as a subsidiary reaction mechanism, but it is apparently not the principal mode of cross-linking.

## EXPERIMENTAL[20]

*Procedure.*—The hydrocarbon, sulfur, and any other ingredients were heated together in an oil bath thermostatically controlled at 141° ± 0.2°, with stirring, in an atmosphere of purified nitrogen. The reaction mixture was left overnight at 0° C, then cooled to −20° C to crystallize out as much free sulfur as possible, and filtered rapidly. The filtrate was subjected to fractional distillation, and all volatile fractions (at 1 mm.) were analyzed for sulfur to obtain an overall yield of cyclic sulfide, since dihydromyrcene and its cyclic sulfide are not readily separable. When soluble accelerator-transformation products, or stearic acid, were present, a benzene solution of the nonvolatile portion was passed through an alumina column, it having been found that hydrocarbon solvents elute dihydromyrcene polysulfides almost quantitatively in unchanged condition. A small portion (*ca.* 0.2 gram) of the eluted polysulfide was treated with aqueous sodium sulfite at 100° C for 2 hours, the sulfur so removed giving an approximate estimate of the free sulfur present, since the amount of polysulfide sulfur removed from dihydromyrcene polysulfide under these conditions is not large, and is known with reasonable certainty[14]. The observed composition and yield of polysulfide were then corrected for the amount of free sulfur present.

*Experiments 1–3* (*Table I*).—Dihydromyrcene (50 g.) and sulfur (5 g.) in 1½, 3 and 6 hours at 141° C yielded respectively, 0.34 g., 0.91 g., and 1.66 g. cyclic sulfide, together with 1.9 g., 4.0 g., and 4.8 g. polysulfide. (Found: C, 57.8; H, 8.3; S, 33.9%.) When zinc oxide (2.5 g., Experiment 4) was also present, the respective yields in 3 hours were 2.1 g. cyclic sulfide and 6.4 g. polysulfide. (Found: C, 67.15; H, 9.85; S, 23.0%.)

*Experiments 5–11, 14.* (*Mercaptobenzothiazole acceleration*).—Experimental details are given below in tabular form, each experiment being run for 30 minutes at 141° C.

*Experiments 12, 15.* (*Benzothiazyl disulfide acceleration*).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g), zinc propionate (0.25 g.) and benzothiazyl disulfide (1 g.) heated for 30 min. at 141° C, yielded less than 0.5 g. reaction product after removal of unchanged hydrocarbon. The addition of 0.2 g. benzoyl peroxide before heating gave the same result. When 0.5 g. tetramethylammonium stearate was added, there resulted 0.37 g. cyclic sulfide and 3.45 g. polysulfide.

*Experiments 16, 17.* (*Diphenylguanidine acceleration*).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g.), zinc propionate (0.25 g.), and diphenylguanidine (0.5 g.), heated for 45 minutes at 141° C, yielded only a trace of cyclic sulfide, but gave 3.9 g. polysulfide. (Found: C, 60.5; H, 9.0; S, 30.5.) Decreasing the sulfur content to 2 g. reduced the yield of polysulfide to 2.2 g. In both experiments 0.7 g. of zinc sulfide was formed.

*Experiments 18, 19.* (*Zinc diethyldithiocarbamate acceleration*).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g.) and zinc diethyldithiocarbamate (0.25 g.) yielded after 15 min. at 141° C, 0.73 g., cyclic sulfide and 3.6 g. polysulfide. (Found: C, 62.35; H, 9.15; S, 28.45.) When heated for a longer period (one hour) at a lower temperature (100° C), the yields were 0.54 g. cyclic sulfide and 2.9 polysulfide.

*Experiment 20.* (*Tetramethylthiuram disulfide acceleration*).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g.), zinc propionate (0.25 g.) and tetramethylthiuram disulfide (0.25 g.), heated for 20 minutes at 141° C, yielded 0.4 g. cyclic sulfide and 3.25 g. polysulfide. (Found: C, 60.5; H, 8.7; N, nil; S, 30.8.)

*Experiment 21.* (*Reaction of tetramethylthiuram disulfide with dihydromyrcene*).—Dihydormyrcene (50 g.), zince oxide (2.5 g.), zinc propionate (0.25 g.) and tetramethylthiuram disulfide (1.5 g.) were heated together for 30 minutes at 141° C. On cooling, a yellow crystalline material separated. The mixture was frozen as in previous experiments, and the filtered solids were extracted successively with benzene and acetone. The benzene extract yielded the intensely yellow tetramethylthiuram monosulfide, m.p. 102–3°, mixed m.p. 103° with authentic specimen, together with zinc dimethyldithiocarbamate m.p. 243°, mixed m.p. 243° with authentic specimen. The acetone extract yielded only zinc dimethyldithiocarbamate. Distillation of the filtered reaction product yielded less than 0.1 g. of cyclic sulfide, together with 1.5 g. of nonvolatile oil which was separated by passage through alumina into two components, eluted, respectively, with benzene and with benzene containing 1% ethanol. The former was a colorless oil (0.6 g.). (Found: C, 74.3; H, 10.8; N, nil; S, 14.4; Zn, nil) and the latter was a brown gum (1.0 g.). (Found: C, 56.8; H, 8.6; N, 5.2; S, 28.1; Zn, nil.)

*Thermal decomposition of tetramethylthiuram disulfide.*—The sample (0.1 g.) was heated in a reaction vessel of the type described by Bolland[21] for active hydrogen determination. The liberation of carbon disulfide was followed by

measurement of its vapor pressure, and also colorimetrically by condensing it into a piperidine-copper oleate reagent[22]. The latter method confirmed the reliability of the vapor-pressure measurements. The amount of carbon disulfide evolved per minute at 140° C was 0.4% of that theoretically available and in 1 hour 30% of the theoretical carbon disulfide had been liberated. At 100° C only 0.03% of the theoretical carbon disulfide had been liberated in 1 hour. Yet in presence of rubber (0.35 g. rubber with 0.0177 g. accelerator, deposited from a solution) 4% of the theoretically available carbon disulfide was liberated in 1 hour at 100° C, and 40% in 1 hour at 140° C. (Found: S combined with rubber, 0.5%.) In the presence of the rubber a trace of hydrogen sulfide was formed, and the measured vapor pressure of the carbon disulfide was suitably corrected. To ascertain the amount of hydrogen sulfide formed, the evolved gases were condensed into methyl magnesium iodide and the hydrogen sulfide was estimated as methane.

*Influence of water on mercaptobenzothiazole acceleration (Table III).*— Samples of a rubber mix (rubber 100, sulfur 3, zinc oxide 5, stearic acid 1, MPC black 30, mercaptobenzothiazole 0.75) were, respectively, dried over calcium chloride, or supended in air saturated with water vapor at 15–20° C for four weeks. Portions were subsequently press-cured according to standard practice at 141° C.

## SUMMARY

Cyclic sulfides are to a large extent secondary products of the reaction of primarily formed intermolecular polysulfides with polyisoprene hydrocarbon, and undue prolongation of the time of reaction of sulfur with polyisoprenes favors cyclic sulfide formation and so reduces the cross-linking efficiency of the sulfur. Various accelerating substances markedly increase the cross-linking efficiency, either by permitting shorter reaction times to be employed, or by promoting a cross-linking rather than a cyclizing reaction of the sulfur. Thiuram disulfide accelerators in the absence of sulfur bring about cross-linking, the linkages being of C—S—C type rather than C—C.

## ACKNOWLEDGMENT

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## REFERENCES

[1] Farmer and Shipley, *J. Chem. Soc.* **1947**, 1519.
[2] Bloomfield and Naylor, *Proc. XIth Intern. Congr. Pure and Applied Chem.*, **1947** (in press).
[3] Kemp and Selker, *Ind. Eng. Chem.* **39**, 895 (1947).
[4] Bloomfield, *J. Chem. Soc.* **1947**, p. 1547.
[5] Bloomfield, *J. Polymer Sci.* **1**, 312 (1946); Kemp and Selker, *Ind. Eng. Chem.* **39**, 895 (1947).
[6] Armstrong, Little, and Doake, *Ind. Eng. Chem.* **36**, 628 (1944).
[7] Kemp and Selker, *Ind. Eng. Chem.* **36**, 16 (1944); Bloomfield, *J. Soc. Chem. Ind.* **67**, 14 (1948).
[8] Altman, *Ind. Eng. Chem.* **40**, 241 (1948).
[9] McColm and Haefele, *Ind. Eng. Chem.* **40**, 311 (1948).
[10] Martin, *Proc. Rubber Tech. Conf. London*, **1948**, p.
[11] Hull, Olsen and France, *Ind. Eng. Chem.* **38**, 1282 (1946).
[12] Gee, *J. Polymer Sci.* **2**, 451 (1947).
[13] Bloomfield, *J. Soc. Chem. Ind.* **67**, 14 (1948).
[14] Bloomfield, *India Rubber J.* **108**, 435 (1945).
[15] Farmer, *Trans. Faraday Soc.* **38**, 356 (1942); Dufraisse and Jarrijon, *Rev. gén. caoutchouc* **20**, 155, 177 (1943).
[16] Bruni, *India Rubber J.* **62**, 89 (1921).
[17] Braun and Weissbach, *Ber.* **63**, 2896 (1930).
[18] Midgley, *Ind. Eng. Chem.* **26**, 1200 (1934); Dufraisse and Jarrijon, *Rev. gén. caoutchouc* **20**, 155, 177 (1943).
[19] Shipley, Thesis London, **1946**; Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* **22**, 308 (1947).
[20] The microanalyses were carried out by W. T. Chambers and (Miss) E. Farquhar.
[21] Bolland, *Trans. Inst. Rubber Ind.* **16**, 267 (1941).
[22] South Metropolitan Gas Co., *J. Soc. Chem. Ind.* **56**, 287T (1937).

# LIGHT PHENOMENA ON ELONGATING VULCANIZED RUBBERS *

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## INTRODUCTORY

As far back as 1934, W. C. Smith, Chief Chemist, Callender's Cable and Construction Co., Ltd., pointed out to the author a curious phenomenon which he had observed with some vulcanized rubbers. If a thin sample of this rubber was torn in a dark room, it showed distinctly light effects. The sample of vulcanized rubber which showed the phenomenon most distinctly contained lithopone as a filler and accelerator Vulcafor D.A., with a small amount of sulfur.

Smith thought it might have to do with the Russell effect, which at that time had been investigated at the Delft Institute[1].

The author encouraged Smith at the time repeatedly to investigate the phenomenon more closely and to publish at least a note on this remarkable phenomenon, but the subject was dropped for the time being.

During the German occupation in 1943, the author took up a further investigation of this phenomenon, which had not been described in rubber literature as far as his knowledge goes[2]. The black-out made it possible to carry out various tensile and other tests in a perfectly dark room.

In the following paragraphs the results of this investigation are given.

## METHOD OF INVESTIGATION

It seemed advisable first to study under what circumstances the light effect appears.

For this purpose a mix was vulcanized similar to the one originally tested, and with this vulcanized rubber various experiments were carried out in a dark room.

(1) Tensile tests with rings and dumb-bell test-pieces on a Schopper dynamometer at a speed of 30 cm. per minute. During the elongation no light effect was visible, but at break a distinct light phenomenon could be perceived at the surface of break. This was more pronounced with the rings, as their section at break is larger than that of the dumb-bell test-pieces.

(2) High-speed tensile test with the Charpuy apparatus. At the moment of break a light phenomenon was visible, but the experiment was less easy, as it is somewhat difficult to observe the ring breaking at high speed in a dark room.

(3) Tear tests. During tear tests also, a light phenomenon could be perceived. If one cuts a film of about 1 mm. thick of the vulcanized rubber and tears it, the light is quite distinct.

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(4) If a dumb-bell test-piece or a ring is elongated slowly by hand no light is visible but, on elongating quickly, a beautiful light phenomenon appears on the whole surface under elongation.

From these simple experiments it appeared unnecessary to carry out tensile tests on a Schopper machine in dark. The experiments could be carried out with films of vulcanized rubbers, about 1 mm. thick, which were elongated at high speed by hand in a dark room.

## INFLUENCE OF THE COMPOSITION OF THE COMPOUND

Originally it was thought that the choice of the accelerator influenced the phenomenon. A mix consisting only of 100 parts of rubber and 8 parts of sulfur, vulcanized for increasing periods, did not show the phenomenon at all. Then systematically a number of mixings with various accelerators were tried. The compounds and their time and temperature of vulcanization are compiled in Table 1.

TABLE 1

COMPOSITIONS WITH VARIOUS ACCELERATORS

| | | | | | | |
|---|---|---|---|---|---|---|
| Standard crepe | 100 | 100 | 100 | 100 | 100 | 100 |
| Sulfur | 5 | 3 | 3 | 3 | 3 | 2 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | — | 1 | 1 | — | 1 | 1 |
| Hexamethylenetetramine | 1 | — | — | — | — | — |
| Mercaptobenzothiazole | — | 1 | — | — | — | — |
| A-32 | — | — | 1 | — | — | — |
| Diphenylguanidine | — | — | — | 1 | — | — |
| Vulcafor P. | — | — | — | — | 1 | — |
| Tetramethylthiuram disulfide | — | — | — | — | — | 1 |
| Vulcanization temperature (° C) | 147 | 137 | 137 | 147 | 147 | 147 |
| Vulcanization time (minutes) | 20/40 | 15/30 | 20/40 | 20/40 | 10/20 | 10/30 |

None of these compounds after vulcanization showed the phenomenon. With these results in hand it was safe to conclude that the accelerator had nothing to do with the light phenomenon.

As there was still a slight possibility that the light phenomenon in some way had to do with an oxidation, the compounds were all subjected to an accelerated Geer aging test for 7 × 24 hours at 70° C in air and, after that period, tested again. Once again the result was perfectly negative.

After this negative result, it seemed reasonable to suppose that the choice of fillers had something to do with the phenomenon under investigation.

The compounds which are given in Table 2 were mixed and vulcanized.

The results of high-speed hand tests with the vulcanized samples are given in Table 2. In this table and the following ones the results are indicated as follows:

| | |
|---|---|
| − | No effect at all |
| + | Some light effect |
| ++ | Stronger light effect |
| +++ | Very strong light effect. |

The results show that lithopone gives a strong effect, independent of the presence of an accelerator. Barium sulfate (ground) gives a strong effect, in

TABLE 2

MIXINGS WITH LITHOPONE AND BARIUM SULFATE

| | | | | |
|---|---|---|---|---|
| Standard crepe | 100 | 100 | 100 | 100 |
| Sulfur | 8 | 5 | 5 | 5 |
| Diphenylguanidine | — | 1 | 1 | 1 |
| Zinc oxide | — | 5 | 5 | 5 |
| Lithopone | 80 | 80 | — | — |
| Barium sulfate (ground) | — | — | 94 | — |
| Barium sulfate (precipitated) | — | — | — | 92 |
| Vulcanization time (minutes) | 90 | 45 | 45 | 45 |
| Vulcanization temperature (° C) | 147 | 147 | 147 | 147 |
| Light phenomenon | ++ | ++ | +++ | — |

contradistinction to blanc fixe (precipitated barium sulfate), which does not show any effect. From these results one gets the impression that there is a possibility that ordinary fillers show the phenomenon, while on the other hand the reinforcing compounding ingredients may not show a light phenomenon. It seemed worthwhile to follow this line of thought.

In relation to this possibility mixings were made with 20 per cent by volume of various fillers, as compiled in Table 3.

TABLE 3

COMPOUNDS WITH 20 PER CENT BY VOLUME OF VARIOUS FILLERS

| | | | |
|---|---|---|---|
| Standard crepe | 100 | 100 | 100 |
| Sulfur | 3 | 3 | 3 |
| Diphenylguanidine | 3 | 1 | 1 |
| Zinc oxide | 5 | 5 | 5 |
| Whiting (ground) | 60 | — | — |
| Talc | — | 61 | — |
| Dixie clay | — | — | 58 |
| Vulcanization temperature (° C) | 147 | 147 | 147 |
| Vulcanization time (minutes) | 30 | 30 | 30 |
| Light phenomenon | +++ | ++ | + |

The results show that all three fillers give a light phenomenon, especially the vulcanizate with ordinary whiting, which shows a beautiful strong light over its surface during a high-speed hand test.

Subsequently, a number of compounds were mixed with 20 per cent by volume of some reinforcing compounding ingredients, such as zinc oxide, titanium dioxide, magnesium carbonate, and carbon black (Micronex). The results are compiled in Table 4.

TABLE 4

COMPOUNDS WITH 20 PER CENT BY VOLUME OF VARIOUS REINFORCING COMPOUNDING INGREDIENTS

| | | | | |
|---|---|---|---|---|
| Standard crepe | 100 | 100 | 100 | 100 |
| Sulfur | 3 | 3 | 3 | 3 |
| Diphenylguanidine | 1.25 | 1 | 1 | 1 |
| Zinc oxide | 5 | 5 | 5 | 5 |
| Carbon black | 44 | — | — | — |
| Zinc oxide | — | 124 | — | — |
| Titanium dioxide | — | — | 86 | — |
| Magnesium carbonate | — | — | — | 48 |
| Vulcanization temperature (° C) | 147 | 147 | 147 | 147 |
| Vulcanization time (minutes) | 30 | 30 | 30 | 30 |
| Light phenomenon | — | — | — | + |

As Table 4 shows, carbon black, zinc oxide, and titanium dioxide do not show any light phenomenon; only magnesium carbonate shows a slight effect, which may be explained by the fact that, although a reinforcing compounding ingredient, it consists of small needles.

The next set of experiments were carried out with a mix with increasing amounts of ordinary whiting, 10, 20, 30, 40, and 50 per cent by volume. The results are compiled in Table 5.

TABLE 5

COMPOUNDS WITH INCREASING AMOUNTS OF ORDINARY WHITING

| | | | | | |
|---|---|---|---|---|---|
| Standard crepe | 100 | 100 | 100 | 100 | 100 |
| Sulfur | 3 | 3 | 3 | 3 | 3 |
| Diphenylguanidine | 1 | 1 | 1 | 1 | 1 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 |
| Whiting | 30 | 60 | 90 | 120 | 150 |
| Vulcanization temperature (° C) | 147 | 147 | 147 | 147 | 147 |
| Vulcanization time (minutes) | 30 | 30 | 30 | 30 | 30 |
| Light phenomenon | +++ | +++ | +++ | +++ | +++ |

The light effect is very strong with all five compounds; the impression is gained that it increases with increasing proportions of whiting. It seemed interesting also to investigate if compounding materials such as Kalite and Calcene would give the effect similar to whiting. As is well known, Kalite and Calcene are both whitings, which are prepared with stearic acid and are supposed to have a coat of calcium stearate.

The compounds tested have been compiled in Table 6 with their results.

TABLE 6

COMPOUNDS WITH KALITE AND CALCENE

| | | | |
|---|---|---|---|
| Standard crepe | 100 | 100 | 100 |
| Sulfur | 3 | 3 | 3 |
| Diphenylguanidine | 1 | 1 | 1 |
| Zinc oxide | 5 | 5 | 5 |
| Kalite | 60 (20 vol.-%) | — | — |
| Calcene | — | 60 (20 vol.-%) | 120 (40 vol.-%) |
| Vulcanization temperature (° C) | 147 | 147 | 147 |
| Vulcanization time (minutes) | 30 | 30 | 30 |
| Light phenomenon | — | — | — |

As Table 6 shows, vulcanized rubbers with Kalite and Calcene do not show any light effect, in contradistinction to ordinary whiting.

## DISCUSSION OF RESULTS

From the foregoing experiments it is clear that the light phenomenon has a direct relation to the compounding ingredients which are used in the mixing.

Vulcanized rubbers with ordinary fillers, such as barium sulfate (ground), whiting, and talc, show a distinct light phenomenon, whereas compounds with reinforcing compounding ingredients, such as zinc oxide, titanium oxide, and carbon black, do not show any light effect.

As is well known since the investigations of Wiegand[3], ordinary fillers are not reinforcing. The original experiments of Schippel[4] showed that, on elongating the vulcanized rubber, the filler particle does not adhere to the rubber, and the observations of Green[5] brought microscopic proof of this by showing the

vacuoles which appear at both sides of the filler particle. On the other hand, these phenomena could not be observed with the reinforcing compounding ingredients such as carbon black and zinc oxide.

When now looking at the results of this investigation, it seems not unreasonable to suppose that the light phenomenon of the rubber with fillers should be viewed in relation to the behavior of these fillers during extension. The bond between rubber and filler is easily broken, and vacuoles appear at both sides. When two dissimilar materials are rubbed or pressed together and subsequently separated, these materials take opposite charges. It seems likely that, when extending vulcanized rubbers with fillers, the adhesion rubber-filler is broken over an extremely large surface. This leads to opposite charges on a tremendous number of spots, with the result that innumerable discharges occur into the surrounding vacuoles, which all together give the impression of a surface light phenomenon. On the other hand, when experimenting with rubbers with reinforcing compounding ingredients, these do not show the Schippel phenomenon, and during extension the compounding ingredients adhere to the rubber, with the result that no opposite charges develop and no discharge appears.

It is believed that this explanation, as far as reinforcing compounding ingredients are concerned, is rather oversimplified.

The investigation of Depew and Easley[6] indicated that the adhesion of rubber to zinc oxide was rather poor and for that reason small vacuoles, and therefore discharges, could be expected in a vulcanized rubber containing zinc oxide. In 1940 accurate measurements were carried out by Jones and Yiengst[7] on the increase in volume, on extension, of vulcanized rubbers containing various compounding ingredients. Their results certainly do not agree with the simplified theory advanced above. Thus, vulcanized rubber containing titanium dioxide shows an increase of volume which comes near to that of rubber containing whiting as compounding ingredient. One should, therefore, expect titanium dioxide to belong to the filler class, but it behaves as a reinforcing compounding ingredient and shows no light effect in extended rubber.

According to Jones and Yiengst, blanc fixe shows considerable volume increase, but it does not show any light effect. The volume increase of rubber with channel carbon black is very small and is in agreement with no light phenomenon visible in this case.

It seems probable that the light phenomenon, apart from the appearing of vacuoles, depends also on various other factors as, *e.g.*, the speed of elongation, the temperature, and the conductivity of the vulcanized compound.

It may be pointed out that Kalite and Calcene in respect to light effect behave as reinforcing compounding ingredients. This is in agreement with the mechanical behavior of rubber containing these compounds[8].

In conclusion it may be remarked that the light phenomenon of vulcanized rubber with fillers such as whiting is strongest during the first high-speed extension, then diminishes quickly, and after a few extensions no light effect is visible. Probably the light effect appears only where the adhesion of the rubber filler is actually broken and vacuoles appear. The friction of rubber and filler particle which certainly occurs on later extensions does not seem to cause discharges, at least not discharges strong enough to cause a light phenomenon visible to the naked eye. The author believes that these light phenomena are worth studying more accurately, as they may give a line of approach to the behavior of compounding ingredients in rubber.

## SUMMARY

A description is given of a light phenomenon, first observed by W. C. Smith, when carrying out tear tests on some loaded vulcanized rubbers in a dark room.

This phenomenon has been studied more systematically by high-speed extension tests.

It appears that this light effect has nothing to do with the choice of accelerators, but with the compounding ingredients of loaded vulcanized rubbers. In general, those compounding ingredients which belong to the filler class, such as whiting, talc, and ground barium sulfate, show this light phenomenon very distinctly, while vulcanized rubbers with reinforcing compounding ingredients, such as zinc oxide, titanium dioxide, and carbon black, do not show any light effect when quickly extended. In accordance with this, Kalite and Calcene, which behave as reinforcing compounding ingredients, do not show any light phenomenon.

It seems probable, that, on elongating the vulcanized rubbers containing fillers, the adhesion of rubber-filler particle is broken, and electrical charges appear on an extremely large surface, which lead to innumerable discharges into surrounding vacuoles, causing the general light phenomenon observed.


## REFERENCES


[1] Van Rossem and Hessels, *Kautschuk* **9**, 181 (1933); **10**, 4 (1934).

[2] T. R. Dawson of the Research Association of British Rubber Manufacturers has been kind enough to call my attention to notes in the literature on luminescence when insulating tape is unrolled (*cf.* French, *Nature* **115**, 944 (1925); **117**, 903 (1926); Harvey, *Science*, **89**, 460 (1939)). It is difficult to judge whether this luminescence is connected with compounding ingredients, since the writers do not give the composition of the cements on the adhesive tapes, but one certainly gets the impression that the composition is related to luminescence, as French mentions that not all adhesive tapes show the phenomenon.

[3] Wiegand, *India Rubber World* **63**, 425 (1921); **64**, 491 (1922).

[4] Schippel, *India Rubber World* **61**, 20 (1919); *J. Ind. Eng. Chem.* **12**, 33 (1920).

[5] Green, *J. Ind. Eng. Chem.* **13**, 1029 (1921).

[6] Depew and Easley, *Ind. Eng. Chem.* **26**, 1187 (1934).

[7] Jones and Yiengst, *Ind. Eng. Chem.* **32**, 1354 (1940).

[8] See, for example, "Calcene-T, Comparison of Calcene-T with Various Calcium Carbonate Pigments in Natural Rubber", Columbia Chemicals, Pittsburgh.

# TENSILE PROPERTIES OF NATURAL AND SYNTHETIC RUBBERS AT ELEVATED AND SUBNORMAL TEMPERATURES *

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In the literature of rubber chemistry and technology it has become customary to call a rubber heat-resistant when its physical properties, measured at room temperature, are not substantially reduced after the rubber has been exposed to elevated temperatures, for example, 100 or 120° C, for certain periods of time, then cooled to room temperature, and again tested. For the purpose of this paper the term *heat aging* will be used to define this type of testing. With this type of test, synthetic rubbers such as Butyl and Neoprene give results superior to those obtained with natural rubber.

Under actual service conditions at elevated temperatures, however, there is frequently a factor of far greater importance than the heat aging as defined above. To evaluate the serviceability at higher than normal temperatures of a rubber product, such as a tire, it is desirable to know the physical properties of the rubber at those temperatures. These properties are more properly classified as the *high temperature strength* of the rubber. It is obvious, therefore, that these high-temperature strength properties must be determined at the actual temperatures to which the product will be exposed in service.

To judge a material on the basis of its strength, not only the usual tensile strength but also the elongation at rupture must be considered. In tensile product $\left(\text{tensile product} = \frac{\text{tensile strength} \times \text{elongation} + 100}{100}\right)$, both properties are united in one value, and the actual strength at the moment of rupture is indicated.

In this paper we shall, for practical reasons, first consider tensile strength and elongation values separately and then discuss the relation of actual strength and temperature.

## EFFECT OF TEMPERATURE ON TENSILE STRENGTH

The effect of temperature on tensile strength has been reported by various authors[1]. The first two investigations concern only natural-rubber compounds, but the third also includes synthetic rubbers at temperatures between 25 and 80° C. In this paper tests will be described on several natural and synthetic rubber compounds over a range of temperatures from −10 to +120° C. Four natural rubber compounds were tested, *i.e.*, a normal-sulfur vulcanizate, a special low-sulfur vulcanizate, a compound vulcanized with tetramethylthiuram disulfide alone, and a carbon black compound. The synthetic rubbers were tested in pure gum and carbon black compounds (see Table 1).

* Reprinted from the *India Rubber World*, Vol. 121, No. 3, pages 299–302, 313, December 1949. This paper is Communication No. 94 of the Rubber Stichting (Rubber Foundation), Delft, Holland.

TABLE 1

COMPOUNDING CHART

| | Natural Rubber | | | | GR-S | | Neoprene GNA | | Butyl | | Perbunan | | Hycar OR-15 | | 41° F. GR-S (Ultipara) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A† | B | C† | D | | | | | | | | | | | |
| Polymer | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide | 10 | 5 | 5 | 10 | 5 | 5 | 5 | 5 | 3 | 3 | 5 | 15 | 5 | 5 | 3 |
| Antioxidant | 1 | — | 1.5 | 1.5 | 1 | 1 | 2 | 2 | — | — | 1 | 2 | — | — | 1.2 |
| Altax | — | — | — | — | — | — | — | — | — | — | — | — | 1.25 | 1.25 | — |
| Captax | 1 | — | 0.8 | 0.8 | — | — | — | — | 0.5 | 0.5 | — | — | — | — | — |
| DPG | — | — | 0.5 | 0.5 | — | — | — | — | — | — | — | — | — | — | — |
| Vulkacit-AZ | — | — | — | — | — | — | — | — | — | — | 1.8 | 1.8 | — | — | — |
| Tuads | 0.2 | 3 | — | — | 0.2 | 0.2 | — | — | 1.0 | 1.0 | — | — | — | — | — |
| EPC carbon black | — | — | — | 44 | — | 50 | — | 30 | — | 50 | — | 57 | — | 50 | 50 |
| Dibutyl phthalate | — | — | — | — | — | — | — | — | — | — | — | — | — | 20 | — |
| Tricresyl phosphate | — | — | — | — | — | — | — | — | — | — | — | 30 | — | — | — |
| Stearine | 1 | 1 | 1 | 2 | 1.5 | 1.5 | 0.5 | 0.5 | 1 | 1 | 2 | 2 | 1.5 | 1.5 | — |
| Other softeners | — | — | — | 10‡ | — | 8 | — | — | — | — | — | 10 | — | — | 4 |
| Sulfur | 0.5 | — | 1.75 | 2 | 2 | 2 | — | — | 2 | 2 | 1.5 | 1.5 | 1.25 | 1.50 | 2 |
| Extra light magnesia | — | — | — | — | — | — | 4 | 4 | — | — | — | — | — | — | — |
| Santocure | — | — | — | — | 1.2 | 1.2 | — | — | — | — | — | — | — | — | 1.65 |
| Vulcanization in minutes | 30 | 30 | 20 | 20 | 30 | 60 | 15 | 15 | 40 | 60 | 25 | 25 | 30 | 45 | 40 |
| Temperature ° C | 134 | 142 | 142 | 142 | 142 | 142 | 152 | 152 | 152 | 152 | 142 | 142 | 152 | 152 | 142 |
| ° F | 274 | 287 | 287 | 287 | 287 | 287 | 306 | 306 | 306 | 306 | 287 | 287 | 306 | 036 | 287 |

* Low-sulfur compound.
† Normal-sulfur compound.
‡ A natural-rubber vulcanizate without softener also was prepared.

The tests were carried out by mounting a jacketed glass tube, through which a heating or cooling liquid circulates, on an ordinary Schopper testing machine. The sample was therefore not in contact with the heating or cooling liquid, but only with indirectly heated or cooled air. The rate of separation of the jaws of the Schopper machine was 30 centimeters per minute.

Results shown in Figure 1 for pure-gum vulcanizates indicate that for Neoprene and Butyl rubbers, tensile strength decreases very rapidly in the neighborhood of 25° C. The temperature coefficient of tensile strength for these

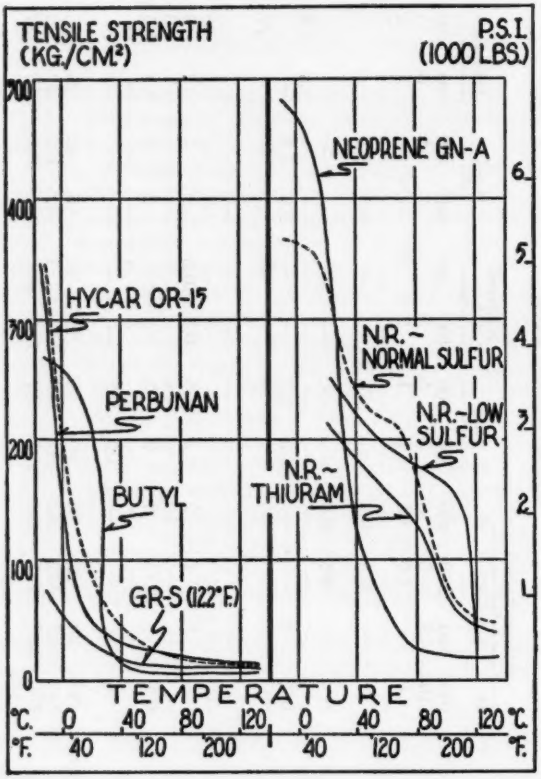


FIG. 1.—Tensile strength as a function of temperature for pure-gum vulcanizates.

rubbers is so high at this temperature that it may be the cause of serious errors in testing if the temperature is not carefully controlled. For nitrile type rubbers (Hycar and Perbunan), this rapid decrease in tensile strength occurs between −10 and +10° C. It appears that even at only 50° C the tensile strengths of these rubbers are very low; the same holds for GR-S; this latter has low tensile strength at any temperature measured above 0° C. The greatest change in tensile strength between −10 and +70° C was registered for Neoprene, which went from 500 kg. per sq. cm. (7,100 lb. per sq. in.) to only 30

kg. per sq. cm.(430 lb. per sq. in.) in this range. All the other synthetic rubbers gave even lower tensile strength figures at 70° C than did Neoprene.

Both the high-sulfur and low-sulfur vulcanizates of natural rubber at 70° C still possess a tensile strength of 180–200 kg. per sq. cm. (2,500–2,900 lb. per sq. in.) and are in this respect far superior to the synthetic rubbers. The normal-sulfur compounds and the thiuram compound lose their tensile strength more rapidly at temperatures above 70° C than does the special low-sulfur compound, which does not show much loss of tensile strength up to 100° C. The natural-rubber thiuram vulcanizate, although decidedly superior in heat aging to the sulfur vulcanizates, has a somewhat lower tensile strength over almost the whole range of temperature tested. This nonsulfur vulcanizate still possesses a high temperature tensile strength, however, of 150 kg. per sq. cm. (2,100 lb. per sq. in.) at 70° C. It is evident that the temperature coefficient of tensile strength of natural-rubber compounds depends on the type of formulation used.

### CARBON BLACK COMPOUNDS

Compounding with carbon black influences the effect of temperature on tensile strength, as is demonstrated in Figure 2. Experiments have shown that

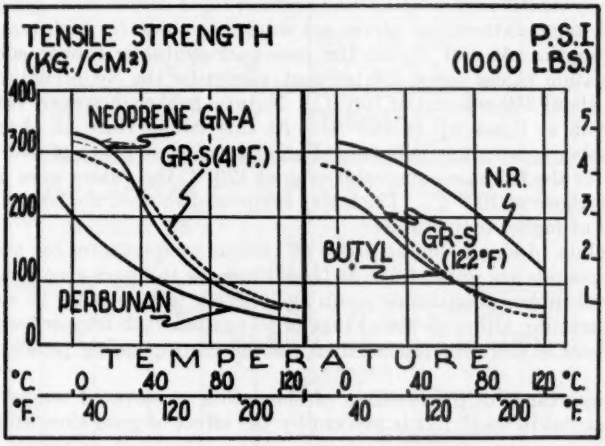


FIG. 2.—Tensile strength as a function of temperature for carbon black vulcanizates.

carbon black in the compound tends to maintain tensile strength at higher than normal temperatures, whereas increasing amounts of softeners or plasticizers have the opposite effect. The Neoprene and Butyl rubber carbon-black compounds in Figure 2 do not contain softeners, and a less pronounced change of tensile strength with temperature, when compared with the pure gum vulcanizates in Figure 1, will be noted.

The other compounds in Figure 2, however, do contain softeners; about 10 parts per 100 for natural rubber and GR-S, and 40 parts per 100 for Perbunan. For natural rubber, the curve is somewhat less steep, but is practically the same as for the normal-sulfur pure-gum compound. For GR-S the curve has changed substantially, since carbon black is necessary to obtain tensile strength

values of practical interest with this synthetic rubber. The general trend of the GR-S curve is about the same as the one for natural rubber, but above 40° C the level is about half that of natural rubber.

"Cold rubber" (GR-S polymerized at 41° C) does not exhibit improved tensile strength at elevated temperatures when compared with regular GR-S; although the tensile strength is somewhat higher at room temperature, this difference almost disappears at 120° C.

The characteristic high decrease in tensile strength when the Neoprene is subjected to elevated temperatures is much less when Neoprene is compounded with carbon black. The tensile strength of Butyl rubber at higher than room temperature is also improved by the addition of carbon black. Perbunan occupies about the same relative position as GR-S. Compounding Perbunan with carbon black improves its tensile strength at elevated temperatures, but at these temperatures it is still not much more than half so strong as natural rubber.

## EFFECT OF TEMPERATURE ON ELONGATION

The effect of temperature on elongation at break for the various rubbers is shown in Figure 3. Elongations at break for pure-gum compounds are given in Figure 3A and for the carbon black compounds in Figure 3B.

All the synthetic rubber compounds exhibit rapid decreases in elongation at break with temperature; the curves are similar to those for high-temperature tensile strength. At 100° C, all the pure-gum synthetic rubber compounds have elongation values below 250 per cent, except for the Neoprene, which has a value of about 300 per cent at 100° C. Natural rubber, however, varies little in elongation at break up to 100° C. At this temperature all three of the natural-rubber compounds still showed an elongation at break of over 600 per cent, and for the thiuram compound even at 120° C the values were not much lower than those at 100° C. The latter compound showed the least change of elongation at higher temperatures.

The values of elongation at break at various temperatures for the carbon black compounds are quite different from those for the pure-gum compounds. The natural-rubber compounds again show much less decrease in elongation with temperature, although the change of elongation with temperature for the other rubbers is less pronounced than for the corresponding pure-gum compounds.

The importance of preservation of elongation at elevated temperatures is not so apparent in itself, but is evident by the effect of good elongation values on high temperature strength properties when calculated as tensile product. Here the greater elongation values for natural rubber at high temperatures would provide higher tensile product values than for the synthetic rubbers, even in any instances where the tensile strength of the synthetic rubber is greater than that of the natural rubber.

### EFFECT OF TEMPERATURE ON TENSILE PRODUCT

The relation between tensile product and temperature is shown in Figure 4 for different pure-gum vulcanizates. It is obvious that the three natural-rubber vulcanizates do not differ much above 40° C; at lower temperatures the normal-sulfur compound exhibits the higher tensile product. The vulcanizates of GR-S and Perbunan show very low values at normal and elevated temperatures, but at subzero temperatures, Perbunan, for example, shows a rapid increase in the tensile product value as the brittle point of the polymer is ap-

proached. This effect is still more evident with Hycar OR-15 and in the Butyl and Neoprene polymers, which have a more regular molecular configuration.

With Neoprene the increase of the tensile product with decreasing temperature is very rapid and reaches the record value of 42.5 kg. per sq. mm. (60,000 lb. per sq. in.) well above room temperature. In fact all of the synthetic pure-gum rubber compounds are very much inferior to natural rubber in their tensile products well above room temperature.

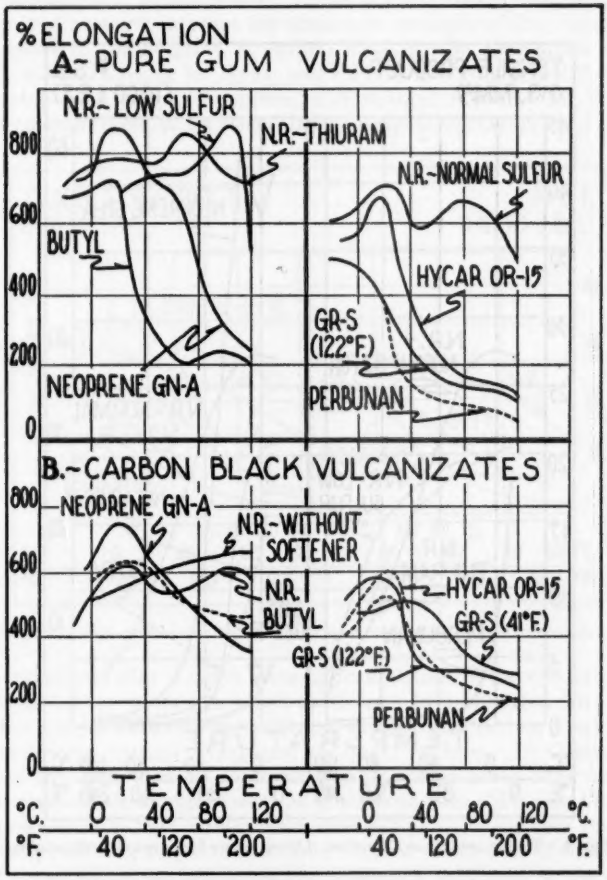


FIG. 3.—Elongation at break as a function of temperature: A—Pure-gum vulcanizates; B—Carbon black vulcanizates.

Though it has not yet been possible in this series of experiments to make tests below −20° C, we may assume that the tensile product decreases again at still lower temperatures. For the normal sulfur compound the work of Wildschut[2] at −253° C supplies proof of this trend. At this very low temperature the tensile product for this natural-rubber compound is only 8 kg per sq. mm.

(11,000 lb. per sq. in.), whereas it amounts to 27 kg. per sq. mm. (38,500 lb. per sq. in.) at room temperature. When the rubber was prestretched at room temperature before testing, the tensile product at −253° C rose to very high values. This result can be explained by assuming that at low temperatures the movement of the chain segments of the rubber molecule becomes too slow in relation to the speed of stretching during the test, and efficient orientation of the chain segments, by which the secondary forces are enabled to exercise their strengthening influence, is hampered, and this hampering results in lower tensile product values at the low temperatures.

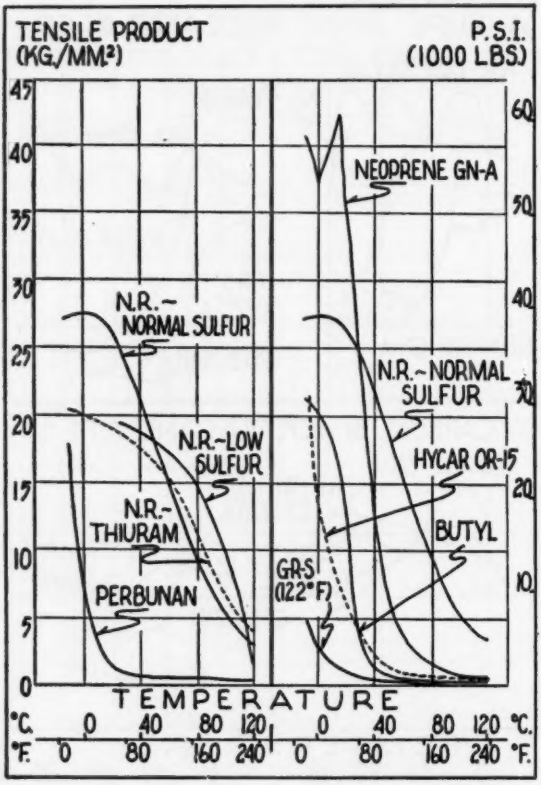


FIG. 4.—Tensile product as a function of temperature for pure-gum vulcanizates.

A certain degree of mobility of the chain segments of a polymer is necessary for the development of maximum strength; at temperatures much higher than room temperature, however, the thermal movements of these chain segments are so vigorous that they destroy the structural order created by orientation. Only in the case of the outstanding regularity of the structure, as found in natural rubber, is orientation and even crystallization maintained at temperatures up to 100° C.

### CARBON BLACK COMPOUNDS

For the carbon black vulcanizates shown in Figure 5 similar considerations are valid, but the effects are somewhat obscured by the grappling action of the carbon black particles. At the lower temperatures the binding forces due to the carbon black result in decreased mobility of the chain segments of the polymers and maximum tensile product, and the point at which the tensile product decreases with increasing temperature is at a higher temperature for the several rubbers than it is with the pure-gum compounds. The effect of carbon black is to shift the maximum tensile product values to higher temperatures; the carbon black does not properly increase the maximum strength of the vulcanizates.

This effect of the addition of carbon black to the compounds on tensile product is most noticeable for Hycar and Perbunan, obvious for GR-S, and not so noticeable with Butyl, Neoprene, and natural rubber. All these three latter polymers crystallize on stretching at room temperature, and it is likely

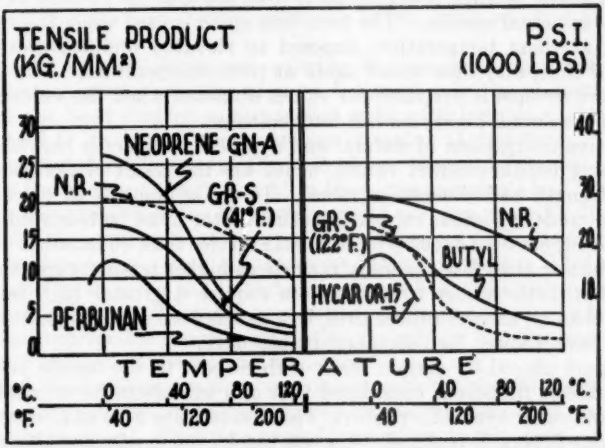


FIG. 5.—Tensile product as a function of temperature for carbon black vulcanizates.

that the crystallites play a much more important part in the ultimate strength of the polymer than do carbon black particles. In accordance with this conclusion, the graphs illustrate the well known fact that carbon black does not properly reinforce natural, Neoprene, or Butyl rubbers. In these cases the strength of the carbon black compounds is decidedly lower than that of the pure-gum compounds, as can be seen from a comparison of Figures 4 and 5.

It is probable also that carbon black does not actually increase the strength of the noncrystallizing polymers; the true effect is really that of increasing the temperature at which maximum tensile product is exhibited to the neighborhood of room temperature. For example, Hycar OR-15 pure-gum vulcanizate with a tensile product of 21 kg. per sq. mm. (about 30,000 lb. per sq. in.) at $-10°$ C has not yet attained its maximum value whereas the carbon black vulcanizate exhibits its maximum tensile product of 13 kg. per sq. mm. (19,000 lb. per sq. in.) at about $+10°$ C. With increases in temperature above room temperature, however, none of the synthetic rubber vulcanizates has a strength comparable to that of natural rubber.

The decided superiority of vulcanizates of natural rubber over those of synthetic rubbers in strength is considered to be due to the regularity of the chain structure of natural rubber, which very easily forms crystallites. The crystal structure embedded in a matrix of homogeneously stretched amorphous material, persistent at very high temperatures and rapidly disappearing with diminishing strain, is responsible for the outstanding physical properties of natural-rubber vulcanizates.

The use of carbon black for those rubbers which are lacking in ability to crystallize, though beneficial for several other properties, is merely providing a substitute for the crystallites in natural rubber, which, as far as strength properties are concerned, is still the best material.

## SUMMARY AND CONCLUSIONS

It is necessary to determine the physical properties of rubbers at relatively high temperatures when products made from them are to be used at such temperatures in actual service. The term *heat aging* is used when the vulcanizate is tested at room temperature, exposed to elevated temperatures for given periods of time, and then tested again at room temperature. The term *high-temperature strength* is proposed for values obtained when the vulcanizates are tested at the actual higher service temperatures.

Effective comparison of natural and synthetic rubbers is best obtained by determining tensile product values, which are the result of the combining of tensile strength and elongation values. In the evaluating of vulcanizates of tire compounds of various rubbers, another factor must be taken into account. Synthetic-rubber tires develop more heat in service than do natural-rubber tires, and the former therefore generally operate at higher temperatures than do the latter. Synthetic-rubber tires therefore require a greater high temperature strength than do natural rubber tires, but, as has been shown, synthetic rubbers actually have a lower high-temperature strength.

The part played by carbon black with respect to the tensile properties of some synthetic rubbers is considered that of a substitute for crystallization in natural and other synthetic rubbers, which substitute does not, however, possess the same favorable features. Carbon black even in noncrystallizing rubbers does not increase strength; it merely shifts the optimum strength value to a higher temperature so that this temperature is in the room temperature range.

The temperature coefficient of strength for Butyl and Neoprene rubbers is so large at room temperature that a few degrees' difference in temperature causes large changes in strength. The tensile strength and elongation at break of these two rubbers decrease sharply between 20 and 40° C.

## ACKNOWLEDGMENT

The reported investigations were a part of the work on the fundamental mechanical properties of rubbers conducted by the research department of the Rubber Stichting at Delft.

## REFERENCES

[1] Van Rossem and van der Meyden, *J. Soc. Chem. Ind.* **45**, 67T (1926); Somerville and Russell, *Ind. Eng. Chem.* **25**, 1096 (1933); Morron, Knapp, Linhorst, and Viohl, *India Rubber World*, Aug. **1944**, p. 521; Wildschut, "Technological and Physical Investigations of Natural and Synthetic Rubbers," New York and Amsterdam, **1946**.

[2] Wildschut, "Technological and Physical Investigations of Natural and Synthetic Rubbers," New York and Amsterdam, **1946**.

# FLOW PHENOMENA IN RUBBER. II. FLOW CURVES FOR GR-S RUBBER *

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In a preceding paper[1] the flow characteristics of natural rubber over a range of temperature were derived from measurements carried out by means of the modified Mooney plastometer employing the biconical rotor of Piper and Scott[2]. In the present paper the results of a comparable study of GR-S are reported.

The rubber used was a standard GR-S, which had been given a preliminary light milling to ensure uniformity over the batch, from which samples were drawn for examination.

*Changes in viscosity during test.*—Owing to changes in apparent viscosity which accompanied the shearing of the GR-S rubber in the plastometer (and which had not been evident in the earlier work with natural rubber) special attention had to be paid to the technique of taking the readings. A typical effect is illustrated in Figure 1. Curve A shows the initial dial readings as a function of the speed of rotation. After these measurements had been taken, the sample was sheared at the highest speed (12 rev. per min.) for 10 minutes. Repetition of the measurements now yielded a lower curve B, showing that the viscosity had apparently been reduced over the whole range. This reduction occurred only on shearing at the higher rates; readings taken at low speeds of rotation were substantially stable over periods up to one hour. In some cases there was an appreciable recovery on resting the rubber, but this was generally only a small fraction of the original reduction.

To avoid these effects, readings were taken with the shortest possible times of rotation, just sufficient time being given for the dial needle to reach a relatively steady position. This time varied, according to the speed of rotation, from 4 or 6 minutes at the lowest speed, to ¼ minute at the highest. Under these conditions it was found possible to obtain reasonably reproducible results, as is indicated in Figure 2, which represents successive runs on the same sample. Generally all the readings at a given temperature were carried out with a single sample of rubber, the reproducibility being checked with repeated readings at the lowest shear rate.

*Form of flow curves.*—From the data obtained at various temperatures the relation between shear stress $s$ and rate of shear $d\sigma/dt$ was calculated. The results being represented on a double logarithmic plot in Figure 3. Some uncertainty attaches to the highest shear rates on account of the difficulties already discussed; the regions of the curves affected by this uncertainty are shown dotted. On the type of plot employed a linear relation is equivalent to the Ostwald-de Waele law:

$$\frac{d\sigma}{dt} = \left(\frac{s}{\eta'}\right)^n \qquad (1)$$

in which $n$ and $\eta'$ are parameters defining the flow properties of the material.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 3, pages 167–171, October 1949.

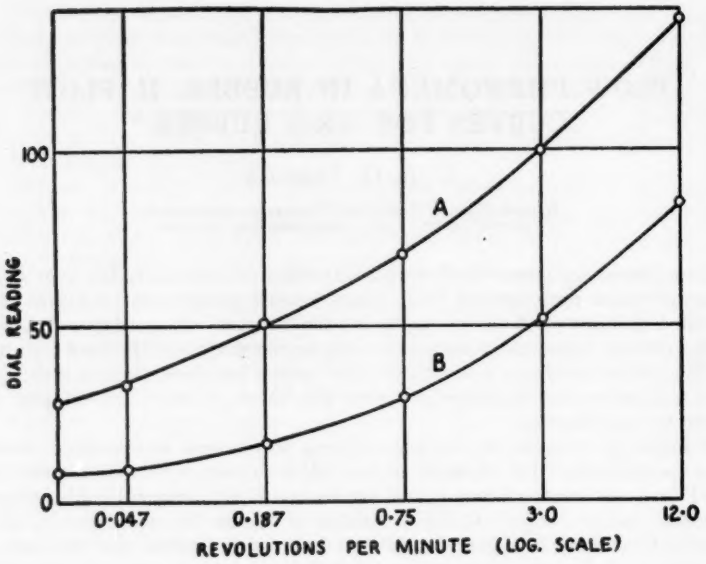
100
50
0
DIAL READING
A
B
0·047
0·187
0·75
3·0
12·0
REVOLUTIONS PER MINUTE (LOG. SCALE)

FIG. 1.

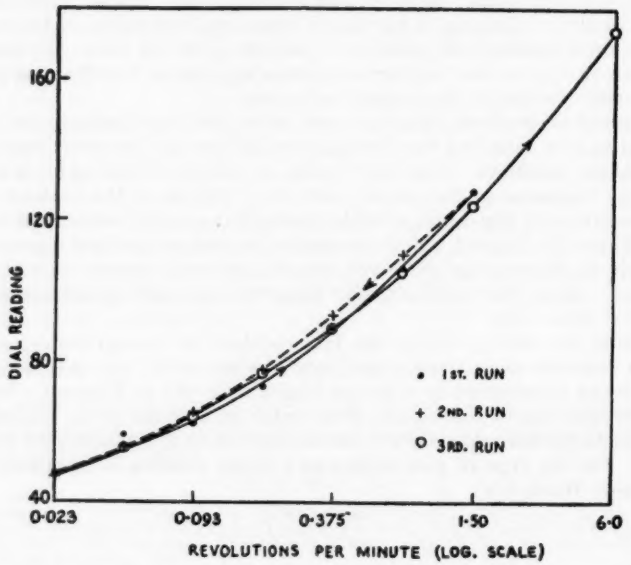
160
120
80
40
DIAL READING
• 1ST. RUN
+ 2ND. RUN
○ 3RD. RUN
0·023
0·093
0·375
1·50
6·0
REVOLUTIONS PER MINUTE (LOG. SCALE)

FIG. 2.

It is seen that the data for all temperatures are in close agreement with the formula (1), though the exponent $n$ decreases slightly, from 4.6 to 4.0, as the temperature rises from 50° to 140° C.

This agreement with the Ostwald-de Waele relation is in contrast to the behavior of the natural rubber previously examined[1]. For this material the log-log plots were not linear. Local values of $n$ obtained by considering the slope of the curves were generally somewhat lower, varying from 1.6 to 3.6 according to conditions. There is at present no evidence as to the practical significance of these differences between natural rubber and GR-S in the technological handling of these materials; it is at least possible that differences in elastic after-effects might prove to be considerably more important than the observed differences in the shape of the flow curves.

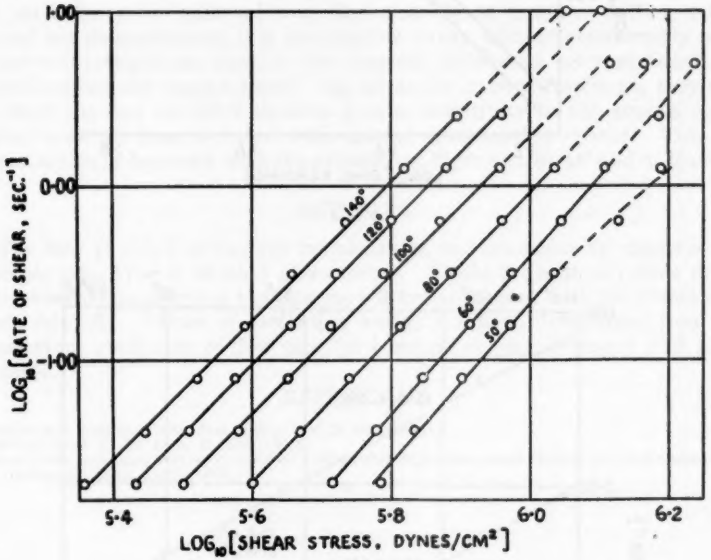


FIG. 3.

*Observations with standard rotor.*—In addition to the data obtained with the biconical rotor, a curve was taken at 100° C, using the standard flat rotor of the Mooney plastometer. These readings are shown in Figure 4 (curve A) and are compared with the values (curve B) calculated from the absolute flow curve (Figure 3) by the method discussed in the previous paper[1]. As in the case of natural rubber, there is some discrepancy between the two curves, amounting to just under 10 per cent in dial readings in the present case. However, it is interesting to note that the slopes of the two curves are identical. This is to be expected on theoretical grounds, since for a material governed by Equation (1) an increase of speed in a given ratio leads to a multiplication of the torque by the same factor, whatever the value of $(d\sigma/dt)$. This factor, which is a measure of $n$, is therefore the same, whether or not the rate of shear is constant over the whole rotor surface. The point is of some practical importance, since it im-

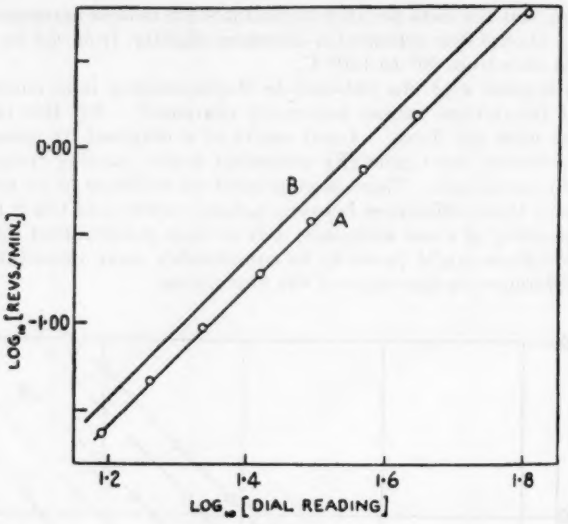
0·00
-1·00
B
A
LOG10 [REVS./MIN.]
1·2
1·4
1·6
1·8
LOG10 [DIAL READING]

FIG. 4.

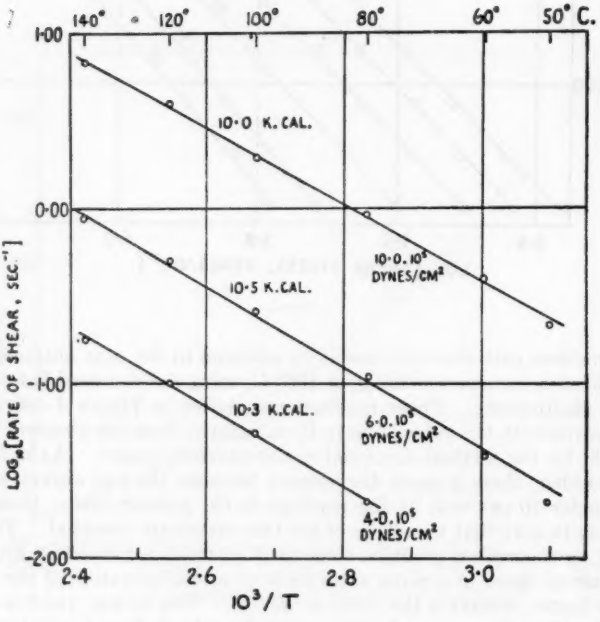
140°
120°
100°
80°
60°
50° C.
1·00
0·00
-1·00
-2·00
10·0 K.CAL.
10·5 K.CAL.
10·3 K.CAL.
10·0.10⁵ DYNES/CM²
6·0.10⁵ DYNES/CM²
4·0.10⁵ DYNES/CM²
LOG10 [RATE OF SHEAR, SEC⁻¹]
2·4
2·6
2·8
3·0
10³/T

FIG. 5.

plies that, if Equation (1) applies, the quantity $n$, which may be taken as a measure of the sensitivity to stress, can be correctly evaluated from measurements with the standard rotor instrument.

*Temperature coefficient of flow rate.*—From the flow curves of Figure 3 the temperature dependence of flow rate, at a given stress, was determined. Data for three different stresses are plotted in Figure 5, using the type of plot previously discussed[1]. The lines are very nearly straight, their slopes yielding values of activation energy averaging 10.2 k.cal. per mole. This value is comparable with that previously found for natural rubber (8.1 kcal. per mole). This agreement in general magnitude is in harmony with the Eyring concept that the unit involved in the flow process is a comparatively short segment of the molecular chain.

*Conclusion.*—On account of the sensitivity of the shape of the flow curves, and particularly the value of $n$ in Equation (1), to previous milling, which Hamm[3] has demonstrated, it is not possible to say without considerably more extensive investigations whether the observed differences between GR-S and natural rubber[1] are characteristic. So far as the present results go, they suggest that the flow in GR-S shows a greater sensitivity to the applied stress (higher $n$-value) than is found with natural (masticated) rubber. This difference is also in harmony with the evidence of Piper and Scott[2] and of Hamm[3].

## SUMMARY

The flow of GR-S at various temperatures was examined by means of the biconical rotor type of Mooney plastometer. Unlike the natural rubber previously studied, the shape of the flow curves was consistent with the Ostwald-de Waele relation. Values of activation energy for flow, determined from the temperature coefficient of flow rate (at constant stress), averaged 10.2 k.cal. per mole.

## REFERENCES

[1] Saunders and Treloar, *Trans. Inst. Rubber Ind.* **24**, 92 (1948).
[2] Piper and Scott, *J. Sci. Instr.* **22**, 206 (1945).
[3] Hamm, Onderzoekingen over het rheologisch Gedrag van ongevulcaniseerde Rubber met de Rotatieplastometer, Meinema, Delft, 1946.

# THE ACTION OF COPPER AND ITS DERIVATIVES ON THE AGING OF RUBBER *

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## INTRODUCTION

Most of the investigations which have been concerned with the action of copper and copper compounds on the aging of vulcanized rubber have brought forth evidence that the deleterious effect is the result of some oxidation phenomenon, but they have left unexplained the mechanism of this action. Kirchhof[1], Esch[2], and Lewin[3] attributed a predominant role to fat acids and resin acids, which they regarded as transforming copper derivatives into metal soaps. According to Bott and Gill[4], these are transformed into cupric oxide through the agency of zinc oxide, which is always present in rubber mixtures. On the other hand, Kawaoka has proposed a different theory[5], according to which the dissociated copper ion is responsible for the deleterious effect of copper. The differences in the behavior of different copper compounds is explained by their greater or less tendency to ionize.

All these investigators studied the effects of copper by mixing copper salts into rubber and then determining, by a comparison of the losses in tensile strength on aging mixtures containing and not containing copper, the extent to which these salts damaged the rubber. Chovin[6] employed a different technique, in that he chose copper salts which are soluble in chloroform, and incorporated them in vulcanized rubber by impregnation. He then measured the resulting autoxidation by a Dufraisse manometer, and calculated for each copper salt a coefficient of acceleration. It should be noted here that most of the studies in this field have been limited to salts of fat acids because of their ease of dispersion in rubber.

In view of this, the work described in the present paper was started by a systematic study of the influence of various inorganic and organic salts of copper. To throw light on the mode of action of these compounds, the parts played by fat acids and by the composition of the vulcanizing system were then studied, and finally a few substances having an anticopper effect were examined.

## SYSTEMATIC STUDY OF THE ACTION OF COPPER SALTS ON THE AGING OF RUBBER

Three different aging tests were employed: (1) accelerated aging in a Geer oven at 70° C, with removal of samples at the end of 4, 8, and 12 days; (2) accelerated aging in an oxygen bomb at 70° C, under a pressure of 20 kg. per sq. cm., with removal of samples at the end of 24, 48, and 72 hours; and (3) natural aging, in which case the samples were stored for 8 months in a drawer.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 26, No. 11, pages 740–744, November 1949. This investigation was carried out in connection with technical instruction at the French Rubber Institute and was presented at the final examination. Because the work had to be finished within a limited time, it is not so comprehensive as it otherwise might have been.

In all three cases, loss in tensile strength was used as a criterion of the deterioration in mechanical properties, but, in addition, these aging tests were supplemented by measurements of the oxidizability at 80° C by means of a Dufraisse manometer, in accordance with the conventional technique.

The different forms of copper which were tested included powdered copper, cuprous and cupric sulfides, cuprous and cupric oxides, cuprous and cupric chlorides, copper sulfate, copper acetate, copper stearate, and copper resinate. In addition, two compounds of types used in the rubber industry were tested, *viz.*, copper phthalocyanine, a color known as Monastral blue, and copper dimethyldithiocarbamate, which is closely related to copper diethyldithiocarbamate, an accelerator of GR-S patented by the R. T. Vanderbilt Company.

## TECHNIQUE

Two pure-gum mixtures which differed only in the accelerator were chosen, with a view to determining whether the copper compounds behaved differently in the presence of an acid accelerator, such as mercaptobenzothiazole, from the way they did in the presence of a basic accelerator, such as diphenylguanidine.

| | | |
|---|---|---|
| Base mixture | Rubber | 100 |
| | Sulfur | 3 |
| | Accelerator | 1 |
| | Stearic acid | 1 |
| | Zinc oxide | 5 |

The copper compounds were incorporated into this base rubber mixture in the same way as were the other ingredients, *i.e.*, by milling, after having made certain that they were fine enough to pass a 200-mesh screen. The amounts added depended on the molecular weights of the copper compounds, and in all cases were such that the copper content was 0.02 per cent and 0.06 per cent, respectively, by weight of the rubber. It was found that, up to 0.02 per cent, the losses in mechanical properties increased in direct proportion to the concentration of copper, but above this percentage they increased less rapidly, as may be seen in Table I, which shows the losses in tensile strength after 12 days in the Geer oven, where the losses are based on the losses of the control containing no copper.

TABLE I

INFLUENCE OF THE COPPER CONTENT ON THE AGING OF A VULCANIZATE

| Percentage of copper as resinate | 0 | 0.006 | 0.01 | 0.02 | 0.04 | 0.06 |
|---|---|---|---|---|---|---|
| Percentage loss in tensile strength | 0 | 9 | 16 | 31 | 36 | 41 |

## RESULTS OBTAINED

*Aging in the Geer oven* (Tables II and III).—For a given concentration of any particular copper compound, the aging depended greatly on the accelerator; thus, with 0.06 per cent of copper in the form of its sulfate, the mixture accelerated by mercaptobenzothiazole had lost 57 per cent of its mechanical strength at the end of 12 days in the oven, whereas the mixture accelerated by diphenylguanidine had lost 75 per cent at the end of only 4 days in the oven.

TABLE II

PERCENTAGE LOSSES IN THE TENSILE STRENGTH OF MIXTURES CONTAINING DIFFERENT COPPER SALTS, AFTER 12 DAYS OF AGING

(Accelerator—mercaptobenzothiazole)

| Copper reagent | Blank without copper | 0.02% copper | 0.06% copper |
|---|---|---|---|
| | 16 | — | — |
| Cuprous sulfide | — | 25 | 32 |
| Cupric oxide | | 26 | 31 |
| Cupric sulfide | | 26.5 | 33 |
| Cuprous oxide | | 28 | 34 |
| Copper powder | | 28 | 37 |
| Cuprous chloride | | 35 | 42 |
| Copper acetate | | 36 | 46 |
| Copper resinate | | 38 | 57 |
| Cupric chloride | | 41 | 53 |
| Copper sulfate | | 47 | 57 |
| Copper stearate | | 47 | 59 |
| Copper phthalocyanine | | 12 | — |
| Copper dimethyldithiocarbamate | | 9 | 14 |

Whatever the accelerator and whatever the copper content, the copper reagents which were tested fell in the same order, and the greater their tendency to ionize, the greater were their harmful effects. In the presence of 0.02 per cent copper, for example, the mixtures accelerated with mercaptobenzothiazole and containing copper powder or the oxides or sulfides of copper lost only 25–28 per cent of their tensile strength after 12 days' aging in the Geer oven, whereas those containing copper salts of easily dissociated acids, such as the chlorides, sulfate, and acetate, lost 36–47 per cent of their tensile strengths. Copper stearate and copper resinate brought about deterioration of the same order or even greater, although they are less ionizable, but their solubility in rubber is greater than that of the other copper compounds.

*Aging in the oxygen bomb.*—These tests were carried out only with mixtures accelerated with mercaptobenzothiazole; with diphenylguanidine, even when the copper content was only 0.02 per cent, destruction was complete in less than 8 hours.

The results, recorded as graphs in Figure 1, show even sharper differences between the deleterious agents than do the Geer oven tests. The most deleteri-

TABLE III

PERCENTAGE LOSSES IN TENSILE STRENGTH OF MIXTURES CONTAINING VARIOUS COPPER COMPOUNDS AFTER FOUR DAYS' AGING

(Accelerator—diphenylguanidine)

| Compound | Blank without copper | 0.02% copper | 0.06% copper |
|---|---|---|---|
| | 25 | — | — |
| Cuprous sulfide | | 44 | 54 |
| Cupric oxide | | 48 | 64 |
| Cupric sulfide | | 50 | 64 |
| Copper powder | | 51 | 54 |
| Cuprous oxide | | 60 | 70 |
| Cuprous chloride | | 77 | 82 |
| Copper sulfate | | 78 | 85 |
| Copper resinate | | 81 | 88 |
| Copper stearate | | 82 | 90 |

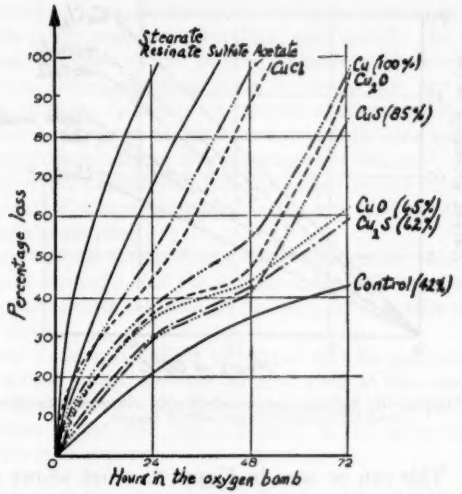


FIG. 1.—Curves showing percentage losses in tensile strength of the mixture accelerated with mercaptobenzothiazole, and containing 0.06 per cent of copper, as a function of the time in the oxygen bomb.

ous agents were the stearate and resinate, which brought about destruction in 24 hours. The salts of easily dissociable acids, the sulfate and chloride, were the next most deleterious, and destroyed the vulcanizates in 48 hours. Finally, the mixtures containing insoluble copper reagents (cuprous oxide and copper powder) were destroyed in 72 hours, whereas the mixtures containing the sulfides retained 35–40 per cent of their tensile strengths at the end of this same 72 hours.

*Natural aging.*—The natural aging tests confirmed the results of the accelerated aging tests.

*Oxidizability tests.*—At first the oxidizability increased rapidly with increase in copper content, then levelled off to a limiting value with further increase in

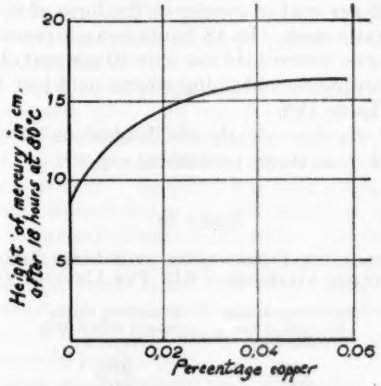


FIG. 2.—Oxidizability tests of mixtures accelerated with mercaptobenzothiazole and containing various concentrations of copper.

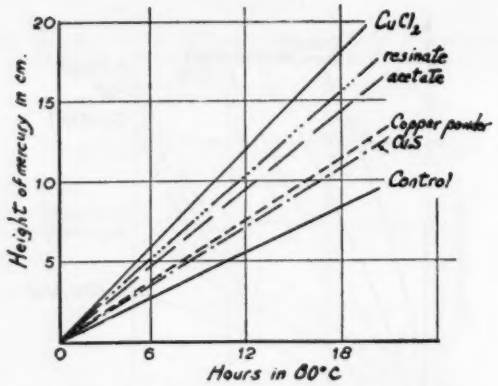


FIG. 3.—Oxidizability tests of mixtures accelerated with mercaptobenzothiazole and containing 0.02 per cent of copper.

copper content. This can be seen in Figure 2, which shows the results with copper sulfate. On the other hand, copper salts of fat acids (resinate and stearate) increased less markedly the rate of oxidation than did cupric chloride (see Figure 3).

In summary, each copper reagent has an action different from other copper reagents. Certain of them, such as the salts of fat acids and the halides, have particularly bad effects, perhaps because of extensive dissociation or because of their relatively great solubility in rubber; others, such as copper phthalogyanine and copper dimethyldithiocarbamate, show no deleterious action.

## STUDY OF THE MECHANISM OF THE ACTION OF COPPER COMPOUNDS

*Influence of fat acids.*—In a first series of tests, the effect of adding fat acids in increasing percentages to the rubber mixture was studied. Stearic acid was chosen for this purpose.

To the mixture accelerated with mercaptobenzothiazole, and already indicated, was added 0.02 per cent of copper in the form of copper acetate, and 2 and 4 per cent of stearic acid. In 48 hours in an oxygen bomb, the control vulcanizate containing no stearic acid lost only 50 per cent of its tensile strength, whereas the two vulcanizates containing stearic acid lost 90 per cent of their tensile strength (see Table IV).

The differences $R_1$-$R_2$ show clearly the deleterious effect of increasing concentrations of fat acid in mixtures containing copper.

TABLE IV

INFLUENCE OF INCREASING PERCENTAGES OF STEARIC ACID ON THE AGING OF MIXTURES CONTAINING 0.02 PER CENT OF COPPER

| Stearic acid (percentage) | Remaining tensile strength of the control $R_1$ | Remaining tensile strength with 0.02% copper: $R_2$ | $R_1$-$R_2$ |
|---|---|---|---|
| 0 | 60% | 50% | 10 |
| 2 | 62% | 42% | 20 |
| 4 | 66% | 10% | 56 |

In a second series of tests, rubber from which its natural fat acids had been removed by preliminary acetone extraction was tested. In this test it was necessary to change the base recipe; in fact, because of the simultaneous elimination of the natural antioxygenic agents in the extraction, the extracted rubber was not stable on storage; furthermore mercaptobenzothiazole can function in its role as accelerator only after transformation into its zinc salt, a transformation which can take place only in the presence of a fat acid. For this reason 0.5 per cent of phenyl-β-naphthylamine was added to the rubber after extraction, and the zinc salt of mercaptobenzothiazole was used as accelerator instead of mercaptobenzothiazole itself.

Under these conditions it was found that the control mixture retained 77 per cent of its tensile strength, and the corresponding mixture containing copper in the form of copper acetate retained 58 per cent of its tensile strength after 12 days in the Geer oven.

Accordingly the deleterious effect of copper and its compounds is manifest even in mixtures which do not contain fat acid, even in the presence of an antioxygenic agent. Hence, even if the deleterious action of copper depends greatly on the concentration of fat acid, the influence of the latter does not explain completely the effects of copper.

TABLE V

INFLUENCE OF COPPER ON THE AGING OF MIXTURES VULCANIZED WITH TETRAMETHYLTHIURAM DISULFIDE

| Mixture | Original tensile strength (kg. per sq. cm.) | Tensile strength after 12 days in Geer oven | Remaining tensile strength (%) | Tensile strength after 72 hours in oxygen bomb | Remaining tensile strength (%) |
|---|---|---|---|---|---|
| No copper | 202 | 198 | 98 | 191 | 94 |
| 0.02% copper (stearate) | 200 | 195 | 97 | 173 | 85 |
| 0.06% copper (stearate) | 203 | 195 | 96 | 154 | 75 |

*Influence of the vulcanizing system.*—In view of the known harmful role of sulfur on aging in general, mixtures containing tetramethylthiuram disulfide as vulcanizing agent were prepared from the following base recipe: rubber 100, tetramethylthiuram disulfide 3, mercaptobenzothiazole 0.5, stearic acid 0.5, and zinc oxide 2 parts. As in the previous experiments, 0.02 and 0.06 per cent of copper were added. The results of the aging tests are shown in Table 5. After 12 days in the Geer oven, the tensile strength values are identical, whether or not the mixtures contained copper.

Under these more severe aging conditions of the oxygen bomb, the action of the copper was nevertheless mild, and was far from that observed with vulcanizates containing sulfur; after 72 hours, the mixture containing 0.06 per cent of copper in the form of stearate retained 75 per cent of its tensile strength; the control mixture 94 per cent. An effort was then made to find out whether this relative insensitivity toward copper is attributable to the absence of sulfur or to the presence of tetramethylthiuram disulfide. To this end two mixtures were prepared, one vulcanized with sulfur and accelerated with tetramethylthiuram disulfide; the other vulcanized with trinitrobenzene. The recipes of these two mixtures were: (1) rubber 100, sulfur 1.5; tetramethylthiuram disulfide 0.5, stearic acid 0.5, and zinc oxide 2 parts; (2) rubber 100, trinitrobenzene 5, and magnesia 10 parts.

In the first case, aging was extremely bad, whether or not the mixture contained copper; hence under these conditions there was no evidence of any

deleterious effect of copper. In the second case, on the contrary, the mixtures aged differently according to whether or not they contained copper. After 12 days in the Geer oven, the control mixture containing no copper retained 65 per cent of its tensile strength, in contrast to only 31 per cent with 0.06 per cent of copper present. The presence of tetramethylthiuram disulfide is, therefore, responsible for the insensitivity toward copper.

Experiments by Jarrijon[7] have shown that tetramethylthiuram disulfide is in part transformed, during vulcanization, into zinc dimethyldithiocarbamate, and it was therefore thought that, in the presence of copper, copper dimethyldithiocarbamate might be formed. This hypothesis seemed all the more plausible since copper dimethyldithiocarbamate was found to have no deleterious effect on aging.

However, with increase in the percentage of copper present, the mixtures vulcanized with tetramethylthiuram disulfide became darker and darker, whereas those to which copper dimethyldithiocarbamate had been added in corresponding proportions were all equally light colored. Furthermore Dubsky[8] has shown that tetramethylthiuram disulfide reacts with metallic salts such as copper chloride, with formation of the compound $4Cu(OH)Cl \cdot 3[(CH_3)_2NC(:S)S]_2$, which forms black crystals, melting at 203° C.

This compound of Dubsky was prepared in the present work, and then the attempt was made to isolate the same compound from the acetone extract of a mixture vulcanized with tetramethylthiuram disulfide and containing 0.06 per cent of copper. A brown or blackish precipitate was obtained, but its melting point was not sharp. This was not surprising in view of the complex nature of the substances extracted by acetone. This would lead oneto conclude that it is not the formation of copper dimethyldithiocarbamate but the formation of some other difficultly soluble organic compound which is responsible for the insensitivity toward copper of vulcanizates accelerated with tetramethylthiuram disulfide.

Another example of insensitivity toward copper is that of reclaimed rubber, as described by Haehl[9]. According to this investigator, proöxygenic agents are without action either on the plasticization or on the aging of reclaimed-rubber mixtures.

Desiring to verify this behavior, mixtures were prepared from two reclaimed rubbers of different origins. One of these reclaimed rubbers was made from a vulcanizate accelerated with mercaptobenzothiazole; the other was made from a vulcanizate cured with tetramethylthiuram disulfide but no sulfur. It was found that copper had a deleterious effect on the vulcanizate containing the first type of reclaimed rubber, whereas the vulcanizate containing the reclaimed rubber made from the mixture cured with tetramethylthiuram disulfide was wholly insensitive to the action of copper.

These experiments indicate that the resistance to copper depends more on the presence of extraneous substances than on the chemical composition of the reclaimed rubber itself.

## STUDY OF THE ANTICOPPER EFFECT

The next experiments were devoted to a study of the protective action obtained by the addition of antioxygenic agents, of metallic deactivating agents (*i.e.*, true anticatalytic agents which react with the metal salt and render it inactive), and of some compounds which might give an indication of what chemical groups are favorable or unfavorable to the anticopper effect sought for.

*Antioxygenic agents.*—The antioxygenic agents were added in a concentration of 0.5 per cent in the standard mixture accelerated with mercaptobenzothiazole, in the presence of, and absence of, 0.06 per cent of copper in the form of copper stearate. Table VI gives the results obtained with Tonox (*p,p'*-diaminodiphenylmethane), Agerite White (*N,N'*-di-β-naphthyl-*p*-phenylenediamine), and BLE Powder (a mixture composed of 65 per cent of a reaction product of a diarylamine with a ketone or aldehyde and 35 per cent of *N,N'*-diphenyl-*p*-phenylenediamine).

TABLE VI

ACTION OF SOME ANTIOXYGENIC AGENTS ON THE AGING OF VULCANIZATES CONTAINING AND NOT CONTAINING COPPER

| Antioxygenic agent (0.5) | Copper (%) | Original tensile strength (kg. per sq. cm.) | Tensile strength after 12 days in Geer oven | Remaining tensile strength (%) | Tensile strength after 72 hours in oxygen bomb | Remaining tensile strength (%) |
|---|---|---|---|---|---|---|
| Control without antioxygenic effect | 0 | 274 | 230 | 81 | 156 | 58 |
| | 0.06 | 233 | 94 | 40 | destroyed in 24 hrs. | |
| Agerite White | 0 | 256 | 225 | 88 | 193 | 76 |
| | 0.06 | 254 | 221 | 85 | 154 | 61 |
| BLE Powder | 0 | 270 | 249 | 92 | 218 | 80 |
| | 0.06 | 275 | 217 | 78 | 148 | 53 |
| Tonox | 0 | 295 | 260 | 88 | 239 | 81 |
| | 0.06 | 298 | 215 | 38 | destroyed in 48 hrs. | |

Agerite White and BLE Powder showed very good protection; Tonox was much less effective.

With respect to classic antioxygenic agents, such as phenyl-β-naphthylamine and aldol-α-naphthylamine, it might be mentioned that the former shows little or no protective power. A mixture prepared from acetone-extracted rubber and containing 0.5 per cent of phenyl-β-naphthylamine is sensitive to the action of copper, as already described; aldol-α-naphthylamine forms with copper a complex which has a deleterious action on aging, for when this complex, as

TABLE VII

ACTION OF DISALYCYLALETHYLENEDIAMINE ON THE AGING OF VULCANIZATES CONTAINING COPPER IN DIFFERENT FORMS

(Accelerator—mercaptobenzothiazole)

| Mixture | Copper (%) | Original tensile strength (kg. per sq. cm.) | Tensile strength after 12 days in Geer oven | Remaining tensile strength (%) | Tensile strength after 72 hours in oxygen bomb | Remaining tensile strength (%) |
|---|---|---|---|---|---|---|
| Control | 0 | 274 | 230 | 84 | 159 | 58 |
| | 0.02% as stearate | 263 | 138 | 47 | destroyed in 48 hrs. | |
| | 0.06% as copper powder | 230 | 145 | 63 | destroyed in 72 hrs. | |
| 0.5% of disalycylalethylenediamine | 0 | 269 | 218 | 80 | 176 | 65 |
| | 0.02% as stearate | 275 | 214 | 77 | 147 | 53 |
| | 0.06% as copper powder | 270 | 211 | 77 | 164 | 60 |

prepared by the method of Kirchhof[10], is added to the standard mixture accelerated with mercaptobenzthiazole, the deleterious effect of copper is manifest.

It is obvious, therefore, that antioxygenic agents are not necessarily anti-copper agents, and that complexes which some of these agents form with copper compounds may still be deleterious.

*Specific protective agents.*—Certain of these products have received commercial names, notably the different so-called copper inhibitors of E. I. du Pont de Nemours & Co. The most recent of this series, X-872-L, is a mixture of 80 per cent of disalycylalpropylenediamine and 20 per cent of an aromatic solvent.

Since, in the work described in the present paper, this commercial copper inhibitor was not available, recourse was had to disalycylalethylenediamine itself. The concentration employed was 0.5 per cent. The anticopper effect was comparable to that obtained with Agerite White, as will be seen in Table VII.

However, it was found that the joint use of disalycylalethylenediamine and classic antioxygenic agents gave the maximum protection against copper, as is evident by the example shown in Table VIII[11].

TABLE VIII

ACTION OF A MIXTURE OF DISALYCYLALETHYLENEDIAMINE AND PHENYL-β-NAPTHYLAMINE ON THE AGING OF VULCANIZATES CONTAINING COPPER

(Accelerator—diphenylguanidine)

| Mixture | Copper | Tensile strength before aging (kg. per sq. cm.) | Tensile strength after 12 days in Geer oven | Remaining tensile strength (%) |
|---|---|---|---|---|
| Control | 0 | 301 | 74 | 25 |
| | 0.02% as stearate | 265 | destroyed | 0 |
| 0.5% disalycylethylenediamine | 0 | 240 | 72 | 30 |
| | 0.02% as stearate | 238 | 37 | 15 |
| 0.5% disalycylethylenediamine +0.5% phenyl-β-naphthylamine | 0.02% as stearate | 231 | 172 | 75 |

## CONCLUSIONS

Most copper compounds increase the rate of autoxidation of rubber mixtures, *i.e.*, they are proöxygenic agents and acclerate aging to a dangerous extent.

However, copper may occur in a disguised form and have no deleterious action at all. Moreover, the effects vary considerably, even with the same copper compound, according to the composition of the rubber mixture. Thus certain ingredients, notably, tetramethylthiuram disulfide, neutralize the deleterious action of copper, whereas fat acids increase it. Nevertheless, the presence of a fat acid is not indispensable to the process of degradation brought about by copper, as is evident from tests with rubber mixtures in which the natural fat acids were previously removed from the rubber.

From the practical viewpoint, protection against copper can be accomplished effectively by means of certain products such as Agerite White, BLE Powder, and disalycylalethylenediamine, all of which are excellent anticopper agents.

## REFERENCES

[1] Kirchhof, *Kautschuk* **3**, 256 (1927).
[2] Esch, *Gummi-Ztg.* **40**, 2697 (1926).
[3] Lewin, *India Rubber World* **175**, 83 (1926).
[4] Bott and Gill, *Trans. Inst. Rubber Ind.* **19**, 53 (1943).
[5] Kawaoka, *J. Soc. Chem. Ind. Japan* **43**, 225B (1940).
[6] Chovin, *Rev. gén. caoutchouc* **19**, 13 (1942).
[7] Jarrijon, Thesis for Doctor of Engineering, Paris, Dec. 1942.
[8] Dubsky, *Collection Travaux chimiques Tchèques* **11**, 295 (1939).
[9] Haehl, *Rev. gén. caoutchouc* **21**, 168 (1944).
[10] Kirchhof, *Kautschuk* **7**, 7 (1931); RUBBER CHEM. & TECHOL. **4**, 239 (1931).
[11] With a view to determining upon what chemical groups this protection against copper depends, a subsequent study was made of the influence of the COOH and $SO_3H$ groups (by means of gallic acid, digallic acid, and sodium alizarinesulfonate), and of the $NH_2$ group (by means of *o*-aminophenol and *p*-aminophenol). It seems that OH groups in certain positions promote the anticopper effect, whereas the COOH group, $SO_3H$ group, and $NH_2$ group suppress this protective action.

# TEAR RESISTANCE OF VULCANIZED RUBBER *

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## INTRODUCTORY

The importance of the determination of the tear resistance of vulcanized rubber articles is well known and finds its expression in the many papers written about this subject and the many different methods used to measure this magnitude. A general survey of the subject can be found in the papers of Buist[1] Patrikeev and Melnikov[2], and Reinsmith[3].

From the theoretical point of view, the work of Busse[4] in 1934 is still the most important. Busse showed how tear resistance varies with depth of cut and width of the remaining part of the rubber. An explanation was given with the aid of a diagram, showing how stresses are spread over the profile of the sample.

In the present paper, a description will first be given of the method used in the Rubber Research Institute T.N.O. (Delft) for the determination of tear resistance. In a number of cases this method has been compared with the angle tear test, described by Graves[5].

As a result of some experiments, the theory of Busse is extended by the examination of the influence of the thickness of the sample on the tear resistance. Further, measurements have been carried out to find out the elongation of the rubber at the apex of the incision.

## TEST METHOD OF THE RUBBER RESEARCH INSTITUTE T.N.O.

For about five years the Rubber Research Institute T.N.O. has used for the determination of the tear resistance a method by which the incision is simultaneously cut (punched) with the sample. Figure 1 gives a cross-section of the die used for this punching; Figure 2 shows the dimensions of the punched test pieces. In the course of time this method has gradually taken the place of the method Van Wijk[6] used previously in this Institute.

Specimens, according to Figure 2, are torn on the tensile testing machine. The tear resistance in kg. per sq. cm. is found by dividing the force in kilograms by the total area of the remaining rubber in the plane of the incision, expressed in sq. cm. In view of the relation between tear resistance and tensile strength, it is preferable to express tear resistance in kg. per sq. cm. and not in kg. per cm. The work of Buist[1] and Busse[4] points in the same direction. It would certainly be preferable to speak of *tear strength* instead of *tear resistance*, for the magnitude, which is measured in kg. per sq. cm. is a strength and not a resistance. In this paper, however, the author, as customary, uses the term *tear resistance*.

A section along the incision, with the aid of a razor blade, shows the shape given in Figure 3. The curvature at the ends of the incision is not the same for

* Reprinted from the *Proceedings of the Second Rubber Technology Conference*, London, June 23–25, 1948, pages 256–267.

FIG. 1.

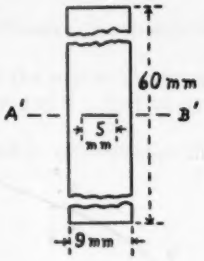


FIG. 2.

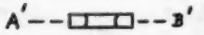


FIG. 3.

FIG. 1.—Cross-section of die used for punching the specimen for tear test.
FIG. 2.—Test piece for tear test (enlarged 2 ×).
FIG. 3.—Cross-section along the incision.

different compounds. A pure-gum compound gives much curvature, whereas a sample of a heavy loaded compound can be cut practically straight.

It seems obvious that the rubber would be cut more straight if the sides of the small knife of the die were also sharpened (at present the side view of the blade is a triangle). It appeared however that the difference was only small and such a knife has the drawback that the corners become severely weakened[7].

Some further remarks concerning this test method will be found later in this paper; it will be indicated in this article as the Delft method.

## INFLUENCE OF THE THICKNESS OF THE RUBBER

As stated already, Busse did not mention the influence of the thickness. Patrikeev and Melnikov[2] gave a diagram of this dependence. The lowest thickness of their samples was 0.5 mm. and extrapolation to zero thickness is, therefore, not possible. For greater thicknesses it is not clear whether the tear resistance becomes independent of thickness or not.

Figures 4 and 5 show the tear resistance, carried out according to the Delft method as a function of thickness. The numbers attached to the curves refer to Table 1, which gives the compositions of the vulcanizates.

For the preparation of the thin samples a round mold was available, and there was a molding flow in the direction of the radius. As a consequence of

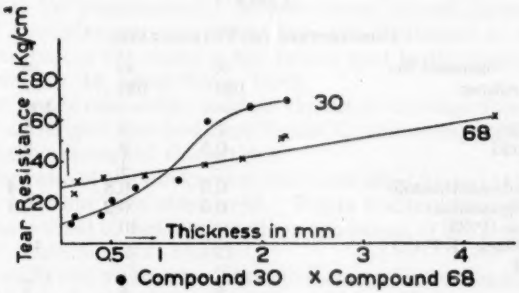


FIG. 4.—Tear resistance as a function of the thickness of the test-piece for compounds 30 and 68.

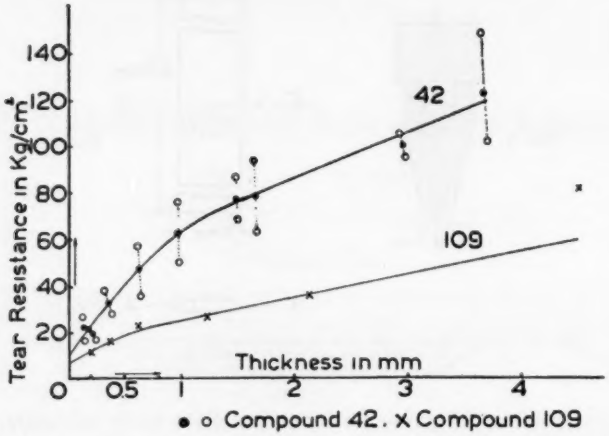


FIG. 5.—Tear resistance as a function of thickness of test-piece for compounds 42 and 109.

this flow, there was an anisotropy in the tear resistance. In agreement with the results of Gurney and Gough[8], the tear resistance of samples cut in the direction of the radius was lower than the resistance of samples cut perpendicularly to the radius.

Care was taken for sufficient plateau effect so that difference in state of vulcanization between slabs of different thickness could not be the cause of erroneous results.

With compound No. 30, the first series with varying thickness, molding anisotropy was not sufficiently taken into account. With small thicknesses, for which this experiment was specially carried out, the differences caused by anisotropy were not large. The other values are a sufficiently exact average. Compound No. 42 showed strong anisotropy. The results are given in Figure 5, separately for tear resistance in the direction of the radius and at right angles with the radius (circles); the curve has been drawn through the average (points).

The anisotropy of the compounds 68 and 109 was negligible. A greater accuracy in making these curves did not seem important, as the shape of the

TABLE 1

COMPOSITION OF VULCANIZATES

| Compound No. | 30 | 42 | 68 | 109 |
|---|---|---|---|---|
| Natural rubber | 100 | 100 | — | 100 |
| GR-S | — | — | 100 | — |
| Zinc oxide | 1 | 5 | 5 | 5 |
| Stearic acid | 0.5 | 2 | 2 | 2 |
| Paraflux | — | 4 | 4 | — |
| Mercaptobenzothiazole | 0.5 | 0.8 | 1.4 | 0.5 |
| Diphenylguanidine | 0.5 | 0.2 | 0.4 | 0.2 |
| Soft black (P-33) | — | 40 | — | — |
| Carbon black (E.P.C.) | — | — | 40 | — |
| Silene-EF | — | — | — | 45 |
| Sulfur | 2 | 2 | 2 | 2 |
| Vulcanization, temperature (° C) | 122 | 138 | 143 | 147 |
| Vulcanization time (minutes) | 20 | 30 | 30 | 30 |

curve depends greatly on the compound used. Here only the general course of these curves will be discussed.

For this purpose a small element of the rubber at one end of the incision is considered, having dimensions of $\Delta x$, $\Delta y$, and $d$. $\Delta x$ and $\Delta y$ are very small, and $d$ is the thickness of the sample.

Stretching causes $\Delta y$ to increase, and in consequence there may be:

(1) a decrease of $\Delta x$
(2) a decrease of $d$
(3) tearing

As long as no tearing takes place, possibilities 1 and 2 have to be considered. Measurements were carried out with samples, prepared according to the principle of the method described above, only using larger dimensions. The width of these samples was 5 cm., the length of the incision was 3 cm. The incision was made with a razor blade.

The experiments made clear that factor 2 is far more important than factor 1. This can be understood with the aid of Figure 6.

Figure 6B shows the incision of Figure 6A under stress. The incision becomes wider and shorter.

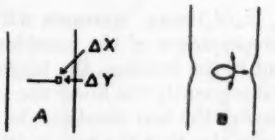


FIG. 6.—Incision changing in shape during tear test.

The considered element is pulled a little to the left and, in turn, pulls at the rubber to its right, but with less effect of displacement. A reaction force pulls the element to the right, so a diminution of $\Delta x$ is counteracted. On the contrary, there is practically no reaction force working against a diminution of the thickness at this point. The hole, formed at the end of the incision, can easily be seen after a little stretching of the sample. These phenomena increase with increasing width of the rubber to the right of the element and with diminishing thickness of the sample or, in general, with the increasing ratio width divided by thickness ($b/d$).

After stretching further the $x$-component of the force becomes smaller in comparison with the $y$-component. Measurements proved, however, that the diminution of $d$ remains more important than the diminution of $\Delta x$. Figure 7 shows the alteration of the shape of the rubber next to the incision for a testpiece of mixture No. 42, about 5 mm. thick.

The figures beside each curve indicate the range of elongations examined of a neutral part of the specimen (compare Figure 12; the average of the elongation of $a$ and $b$ is taken as normal elongation).

Further, the ratio of the thickness at the outer side ($d_0$) and at the inner side ($d_i$) of the element has been considered. Figure 8 shows this ratio $d_0/d_i$ as a function of the normal elongation for three specimens of different thicknesses (compound 42 containing soft black).

This ratio tends to a maximum. At higher elongations the samples of Figure 8 tore somewhat in the direction of stretch, so further determinations were not possible.

Later measurements showed that this maximum value of $d_0/d_i$ may remain constant over a long range, sometimes from a very low elongation, and always up to the last determination before tearing. A set of samples of another carbon black mixture, with increasing periods of vulcanization, thickness 5 mm., gave the following values of $(d_0/d_i)$ max.: 1.62, 1.65, 1.59, and 1.62. The same experiment with a pure-gum compound gave the values 1.58, 1.61, 1.59, and 1.61. The constancy of this factor is a curious fact.

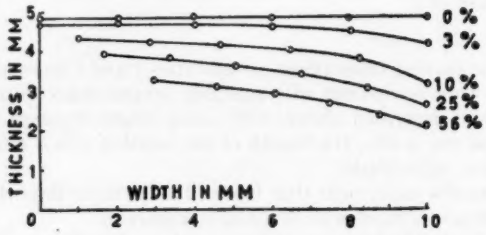


FIG. 7.—Change in shape near to the incision with increasing normal elongation.

Figure 8 shows that $(d_0/d_i)$ max. increases with decreasing thickness, as could be expected as a consequence of the considerations given above. The deeper the hole at the end of the incision, the bigger the concentration of the forces at this point and consequently the lower the value of the tear resistance.

Qualitatively, the course of the tear resistance as a function of the thickness is now clear. It can be seen also that the tear resistance does not become zero for zero thickness, as the curve of Patrikeev and Melnikov[2] suggests. With a decrease of $d$ always a diminution of $\Delta x$ is possible.

Figure 8 shows that, with an original thickness of 10 mm. $(d_0/d_i)$ max. = 1.33. Before stretching, this element was a square of 10 mm. × 10 mm. If now, for the samples of 5 mm. and 2 mm. thickness, squares are taken of 5 × 5 mm., and 2 × 2 mm., respectively, bordering on the incision, and the alterations of the thickness at the outer and inner side of these squares are considered, then $(d'_0/d_i)$ max. appears to be 1.35 and 1.39, respectively, this being for the three cases practically the same value.

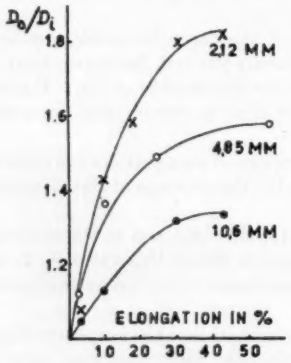


FIG. 8.—Ratio $d_0/d_i$ as a function of the normal elongation.

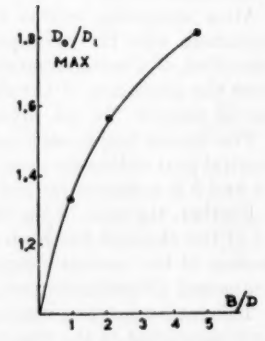


FIG. 9.—Ratio $d_0/d_i$ max. as a function of the ratio $b/d$.

This indicates that the most important factor for these considerations is the ratio of width and thickness of the rubber besides the incision.

It is for this reason that in Figure 9 the values of $d_0/d_i$ max. of Figure 8 are drawn as a function of $b/d$. In these experiments the width $b$ was constant, $b/d$ becomes zero for infinite thickness. Thus, Figure 9 shows that, for infinite thickness, $d_0/d_i$ becomes = 1, or, in other words, there is no concentration of forces at the end of the incision, and the tear resistance becomes equal to the tensile strength.

Figure 10 shows that, in case of a small value of $b$, the sample is shaped even at low elongations to such a form that the forces at the inner and outer side are practically equal. The ratio $(d_0/d_i)$ max. reached in this case the value of 1.06. When $b$ becomes zero, then the tear resistance is equal to the tensile strength.

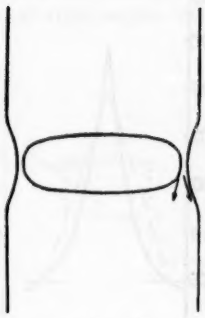

FIG. 10.—Shape of incision with a small value of $b$, when elongating the test-piece.

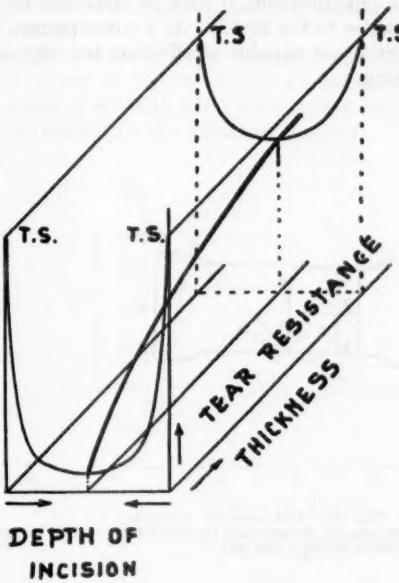


FIG. 11.—Three dimensional diagram of relation between tear resistance and thickness of the sample, depth of the incision, and width each side of the incision.

Busse remarked that the tensile strength in such a case need not have necessarily the same value as the one found in standard tensile tests. It should be realized that tensile strength is not a universal constant, but depends on the shape of the sample and the method of testing. In the next paragraph it is shown, however, that the elongation at the end of the incision at the moment of tearing reaches practically the same value as the ultimate elongation during the tensile test. Thus, the "tensile strength" used in this connection is really comparable with the tensile strength of the standard tensile tests. The figures concerning the relation between tear resistance and thickness can be put together with the influence of width of sample and depth of cut in a three dimensional diagram being an extension of Busse's diagram. The result is shown in Figure 11.

For reasons of simplicity it is accepted that tensile strength does not alter with increasing thickness.

## ULTIMATE ELONGATION AT THE END OF THE INCISION

In this paragraph the question is considered whether the elongation at the point where tearing starts, is equal to the elongation at break of a standard tensile test.

It has been shown that at that point there is a force, acting at right angles to the direction of stretch (see Figure 6). The question should now be answered whether this force can affect the ultimate force and elongation in the direction of stretch. The conclusion of Flint and Naunton[9] from their experiments concerning stretch in two directions is that, "having stretched the rubber to the limit in one direction, it may be stretched to a similar extent in a direction at right angles to the first." As a consequence, the small force in the case of the tear test is not capable of effecting the ultimate elongation in the direction of stretching.

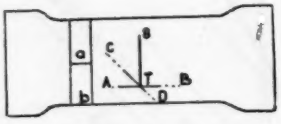


FIG. 12.—Test-piece for measuring the ultimate elongation at the end of the incision during a tear test.

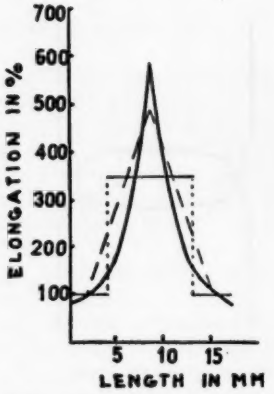


FIG. 13.—Relation between the measured elongation and the length of stretched piece.

With the aid of the specimen shown in Figure 12, measurements of the elongation were performed as near to the end of the incision as possible. The incision is indicated by ST. The average of the elongation of *a* and *b* is the normal elongation used in the present paper.

For the first experiment, lines were drawn on a test-piece of Compound 109 (20 per cent by volume Silene EF) at distances of 2 mm., parallel to, and at right angles with, AB. The alterations of length, width, and thickness were measured. The elongation at break of the same compound determined with Schopper rings, was 630 percent; with dumb-bells of 3.2 mm. width 680 per cent.

During various experiments, the middle part of 2 mm. of AB could be stretched to 9 mm. (350 per cent elongation), the next 2 mm. to the left and to the right to 4 mm. (100 per cent elongation). These figures show that the elongation diminishes very quickly with increasing distance from the point T. However, the highest elongation can be estimated by extrapolation.

In Figure 13 the elongation is plotted against the length of the stretched pieces. Using linear extrapolation (dotted lines), the highest elongation still remains lower than 500 per cent. It is clear, however, that a sharper extrapolation should be used. In that case the highest value is at least between 500 and 600 per cent, as Figure 13 shows.

By drawing circles with T as a center, the elongation can be measured in all directions, starting from T. In stretching, the straight line AB is curved and the direction of highest elongation appeared to run more to the middle of the test-piece. Three circles were drawn with a radius of 1, 2, and 3 mm., center T. In the direction of the highest elongation, the values found were 410, 120, and 80 per cent. Extrapolation yields a value between 600 and 700 per cent for the elongation at point T. However, this experiment is not quite reliable. A very small tear displaces the center of the circles and causes the values to become too high. Measuring along the straight line, it is always possible to measure along a parallel line through the new point T.

It was mentioned before that AB is not the most favorable direction for these determinations. The results, given in Figures 14 and 15, were obtained by measurements along CD at an angle of 45° with AB. In this case, lines were drawn at right angles with AB with the aid of the following method.

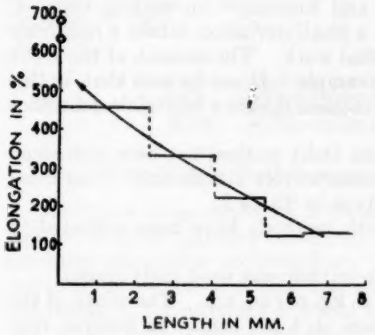


FIG. 14.—Extrapolated ultimate elongation along the CT line.

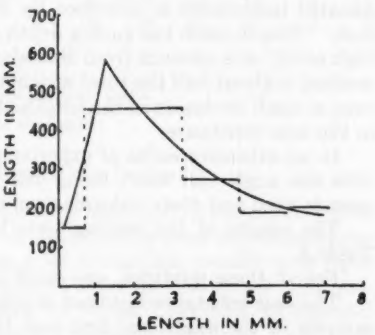


FIG. 15.—Extrapolated ultimate elongation along CD line.

The dumb-bell test-pieces were stretched 3 to 4 times their original length. In this elongated condition lines were drawn at right angles to AB at distances of 1 mm., which, after relaxation, was reduced to 0.3 mm. Now the incision was made.

Obviously, these lines did not make right angles with CD. As a consequence of this fact the picture is distorted after stretching. However, with care it was possible to measure the elongation in the direction of CD. In Figure 14 the elongation in the direction of TC is shown; Figure 15 shows that, in the direction from T to D, the elongation diminishes very quickly. In this case no sharp extrapolation is necessary.

The highest value of the elongation which was actually measured amounts to 450 per cent; extrapolation yields a value between 500 and 600 per cent. The difference from the ultimate elongation with tensile tests of 630 to 680 per cent can reasonably be explained by the following arguments:

(1) The determinations are not made at the moment of tearing but a short time before.
(2) When observing the process of tearing under a microscope, it can be seen that this process has a strong resemblance to the tearing of a bunch of fibers one by one. At a certain moment only one fiber needs to have the ultimate elongation.

On account of the experimental results and these two arguments, it seems therefore acceptable that, at the end of the incision locally an elongation is obtained, practically equal to the ultimate elongation of the standard tensile tests.

It should be emphasized that, as a consequence of this sharp localization of ultimate elongation, the value of the tear resistance is only partly determined by the value of the tensile strength. The influence of other factors (especially the modulus) should be the subject of future experiments.

## COMPARISON BETWEEN ANGLE TEAR TEST AND THE DELFT METHOD

The tear test already described has, compared with most other methods, the advantage of simplicity. Punching the test-piece and the incision are carried out in one act. For the crescent tear test, for example, a rather complicated instrument is described by Buist and Kennedy[10] for making the incision. This incision has such a depth that a small deviation causes a relatively high error, as is obvious from Busse's original work. The incision of the Delft method is about half the total width of the sample. It can be seen that, in this case, a small deviation in the length of the incision makes a negligible difference in the tear resistance.

In an extensive series of experiments the Delft method has been compared with the angle tear test[5], being also a comparatively simple one. The compounds used and their vulcanization are given in Table 2.

The results of the tearing tests by both methods have been collected in Table 3.

For all these mixtures, one stock of raw rubber was used (pale crepe).

The tear resistance has been expressed in kg. per sq. cm. The width of the samples of the angle tear test was 13.2 mm. ± 1 per cent. In general, four samples were taken for the angle tear test, 5 for the Delft method (these test-pieces are smaller) and three for the tensile test. The figures obtained were corrected for a thickness of exactly 1, 2, and 3 mm.

The deviation in percentage is calculated as follows. The mean deviation is expressed as percentage of the average. The figures so obtained are again averaged over a set of values, for instance, a whole mixture.

TABLE 2

COMPOUNDS USED FOR COMPARATIVE TEARING TESTS

| Compound No. | 161 | 167 | 232 | 271 | 243 | 272 | 273 | 279 | 285 |
|---|---|---|---|---|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Benzothiazoyl disulfide | 0.5 | 0.6 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 | 0.6 | 1.4 |
| Diphenylguanidine | 0.5 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.4 |
| Age-Rite | | | 1 | 1 | 1 | 1 | 1 | | 1 |
| Carbon black (EPC) | | | | 20 | 40 | 60 | 80 | | 40 |
| Dixie clay | | | 60 | | | | | | |
| Silene-EF | | 45 | | | | | | | |
| Factice | | | | | | | | 10 | |
| Sulfur | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Vulcanization, temperature (° C) | 147 | 147 | 147 | 147 | 147 | 147 | 147 | 147 | 147 |
| Vulcanization time (minutes) | 20 | 20 | 40 | 40 | 40 | 40 | 40 | 30 | 15 |

TABLE 3

RESULTS OF TEARING TESTS

| Compound No. | 161 | 167 | 232 | 271 | 243 | 272 | 273 | 279 | 285 |
|---|---|---|---|---|---|---|---|---|---|
| Angle (kg. per sq. cm.) (1 mm.) | 17 | 15 | 17 | 16 | 29 | 38 | 10 | 16 | 57 |
| Delft (kg. per sq. cm.) (1 mm.) | 67 | 26 | 20 | 17 | 67 | 77 | 25 | 20 | 112 |
| T.S. | 363 | 230 | 222 | 246 | 283 | 242 | 173 | 272 | 335 |
| Angle (% T.S.) | 5 | 7 | 8 | 7 | 10 | 16 | 6 | 7 | 17 |
| Delft (% T.S.) | 19 | 11 | 9 | 7 | 23 | 32 | 14 | 9 | 33 |
| Angle (% Delft) | 25 | 58 | 85 | 94 | 43 | 49 | 40 | 80 | 51 |
| Angle (kg. per sq. cm.) (2 mm.) | 24 | 25 | 16 | 17 | 50 | 37 | 13 | 21 | 70 |
| Delft (kg. per sq. cm.) (2 mm.) | 79 | 51 | 19 | 24 | 95 | 88 | 42 | 21 | 157 |
| T.S. (kg. per sq. cm.) (2 mm.) | 327 | 228 | 212 | 236 | 275 | 247 | 174 | 255 | 334 |
| Angle (% T.S.) | 7 | 11 | 8 | 7 | 18 | 15 | 7 | 8 | 21 |
| Delft (% T.S.) | 24 | 22 | 9 | 10 | 33 | 36 | 24 | 8 | 47 |
| Angle (% Delft) | 30 | 49 | 34 | 71 | 53 | 42 | 31 | 100 | 45 |
| Angle (kg. per sq. cm.) (3 mm.) | — | — | 15 | 20 | 61 | 56 | 21 | 23 | 70 |
| Delft (kg. per sq. cm.) (3 mm.) | — | — | 20 | 33 | 116 | 107 | 58 | 27 | 188 |
| T.S. (kg. per sq. cm.) (3 mm.) | — | — | 193 | 231 | 275 | 238 | 170 | 236 | 334 |
| Angle (% T.S.) | — | — | 8 | 9 | 22 | 24 | 12 | 10 | 21 |
| Delft (% T.S.) | — | — | 10 | 14 | 42 | 46 | 34 | 11 | 56 |
| Angle (% Delft) | — | — | 75 | 61 | 53 | 52 | 36 | 85 | 37 |
| Hardness (Shore-A) | 40 | 47 | 46 | 43 | 56 | 68 | 79 | 38 | 57 |
| M-200 | 8 | — | 29 | 16 | 37 | 72 | 118 | 8 | 32 |
| Deviation % Angle | 4 | 5 | 8 | 8 | 18 | 17 | 18 | 3 | 12 |
| Deviation % Delft | 15 | 13 | 3 | 13 | 13 | 19 | 17 | 9 | 7 |

*Abbreviations*

Angle ....Angle tear test (kg. per sq. cm.).
Delft ....Method Rubber Research Institute (Delft).
T.S. ....Tensile strength (dumb-bell test pieces of 3.2 mm.).
M-200....Modulus at 200 per cent elongation.

From these figures the following conclusions can be drawn:

1.—The average deviation is the same for both methods (11 per cent). This number is rather high as a consequence of the fact that, in these experiments, no attention was paid to molding flow. When a set of samples, parallel or at right angles to the direction of flow, has been punched lower deviations are obtained. For instance, the mixtures of Table 1 yielded the values 7 per cent (Compound 30), 10 per cent (Compound 42), 4 per cent (Compound 68), and 6 per cent (Compound 100) (Delft method).

The small standard deviation for the angle tear test, found by Morris and Bonnar[11] in the case of natural rubber, is in good agreement with the values found for the mixtures 161 and 279, as Morris and Bonnar only used a pure-gum compound.

2.—The influence of the thickness exists to the same extent for both methods.

3.—Using carbon-black mixtures, both methods show the phenomenon of tearing in the direction of stretch.

4.—The difference between the angle tear test and all other tear tests is that the incision is replaced by a V-shaped excision. This makes the concentration of forces less locally. In this respect a shape of the test specimen as given in Figure 16b would be preferable to the one of Figure 16a, used now.

This V-shaped excision has no resemblance to practical cases of tearing. The angle tear test (Figure 16a) lies between an ordinary tear test and a tensile test, though nearer to the side of the first.

The idea of Buist and Kennedy[10], taken over by Morris and Bonnar[11], that the angle tear test is a test of tear initiation, contrary to other tests, which are tests of tear propagation, cannot be supported by the present author. In all

these tests a tear is initiated. Only the tear is a propagation of an incision or excision. If one wants to know the force required to start an incision, quite another method is necessary, *e.g.*, the wire cutting test of Werkenthin[12].

It can be seen from the original figures of Graves that the angle tear test is much more affected by the tensile strength than the crescent tear test.

Comparison of the mixtures 285 and 243 yields another example of this fact. Mixture 285 contains a much larger proportion of accelerators. This is decidedly favorable for tear resistance. The increase of the tensile strength is 17 per cent, that of tear resistance by the angle tear test 40 per cent, and that of the tear resistance by the Delft method 65 per cent.

5.—Comparison of mixtures 279 and 161 shows that the value of the angle tear test is practically unaffected by the addition of factice to the mix, whereas the value obtained with the Delft method is affected distinctly. Hand tearing tests indicate that the latter result is correct.

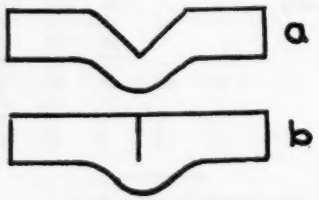


FIG. 16.—Angle tear test.

6.—Comparison of mixtures 167 (Silene EF) and 161 (pure-gum) gives similar results. The angle tear test is not in agreement with hand testing.

7.—For mixture 232 (clay) the value of the angle tear test is practically the same as the tear resistance by the Delft method, whereas in other cases the latter value is nearly always higher. The conclusion is that the result of the first method is not in accordance with the well known very low tear-resistance of a clay mixture.

## SUMMARY

The method now used at the Rubber Research Institute T.N.O. for determining the tear resistance of vulcanized rubber is described in detail.

The tearing test has been studied further. The influence of the thickness of the sample on the tear resistance has been investigated, and some experiments carried out to explain this influence are described.

Further experiments indicate that, at the moment of tearing, an elongation is reached locally which is practically equal to the elongation at break of a standard tensile test.

Comparison of the angle tear test with the above method leads to the conclusion that the Delft method is to be preferred.

## ACKNOWLEDGMENT

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## REFERENCES

[1] Buist, *Trans. Inst. Rubber Ind.* **20**, 155 (1945).
[2] Patrikeev and Melnikov, *Kauchuk i Rezina*, Dec. **1940**, p. 12; RUBBER CHEM. & TECHNOL. **14**, 863 (1941).
[3] Reinsmith, *India Rubber World* **116**, 499 (1947).
[4] Busse, *Ind. Eng. Chem.* **26**, 1194 (1934).
[5] Graves, *India Rubber World* **111**, 305 (1944).
[6] Van Wijk, *Kautschuk* **14**, 2, 26 (1938).
[7] Van Wijk, D. J., private communication.
[8] Gurney and Gough, *Trans. Inst. Rubber Ind.* **22**, 132 (1946).
[9] Flint and Naunton, *Trans. Inst. Rubber Ind.* **12**, 367 (1937); see particularly p. 400.
[10] Buist and Kennedy, *India Rubber J.* **110**, 809 (1946).
[11] Morris and Bonnar, *Anal. Chem.* **19**, 436 (1947).
[12] Werkenthin, *Rubber Age* (N. Y.) **60**, 197 (1946).

# KINETIC STUDY OF THE OXIDATION OF RUBBER I.—SOME OBSERVATIONS IN THE CASE OF RAW RUBBER *

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## INTRODUCTION

The problem of protecting natural rubber against the harmful effects of oxygen is of prime importance. Dufraisse[1] gave in 1937 an excellent exposition of the problem. Since then a number of papers have been published which have dealt with systematic studies of the reaction between rubber and oxygen and the mechanism of antioxidant action. Furthermore, one of us[2] has drawn attention to a special type of protection with the aid of substances called deactivators, which retard the aging of rubber without marked diminution of its oxidizability. The hypotheses advanced as to the way in which these compounds exert their effect have led to a method of improving the aging resistance by means of the combined use of an antioxidant and deactivator[3]. Nevertheless it was useful not only from the theoretical point of view, but from the point of view of subsequent development, to try to elucidate the exact nature of the phenomenon. That is why we have undertaken a kinetic study, hoping that the changes in rate observed under the influence of various factors would furnish some indication of the mechanism of the phenomena. Although the practical end was the protection of vulcanized rubber, we have also been led to examine the case of raw rubber because: (1) raw rubber lends itself better to certain experimental requirements and to purification, and it is indispensable to know as exactly as possible the behavior of the rubber hydrocarbon; (2) the ingredients added for vulcanization, and the modification of structure which the latter introduce, have a greater or less influence on the phenomena studied; (3) the systematic comparison of the results obtained with raw rubber and vulcanized rubber should make if possible to assess the importance and nature of these variations and to determine in what measure the rules established for raw rubber are applicable to vulcanized rubber; and (4) the effect of the deactivator on raw rubber has not yet been studied.

The necessarily restricted scope of the present paper limits the discussion to indicating the principle underlining the experimental technique, together with some of the observations made in the case of raw rubber.

## OUTLINE OF PREVIOUS WORK

There is no intention of giving here a bibliography of the numerous papers dealing with the oxidation of rubber. These, for the most part, have been concerned with vulcanized rubber, so a brief account of some of the principal results obtained from studies on the raw product alone is given. Here it is necessary to distinguish between two different aims: (1) the determination of

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the products resulting from oxidation; (2) the measure of the rates of oxidation and their variations. A knowledge of these two kinds of data is evidently indispensable to an exact understanding of the phenomena, but as the present work contains no results relative to the products of oxidation, the following deals only with those which were concerned with measurement of the oxygen absorption.

It seems that the first measurement of this type was made by Peachey[4]. He deposited a thin film of rubber on the inner surface of a flask by evaporation of a benzene solution, filled the flask with oxygen, and put the system in communication with a graduated burette; in this way he measured the absorption of oxygen at 85° C of ordinary crepe and an acetone-extracted crepe, and showed that, while the presence of the resins has only a slight influence on the total volume of oxygen absorbed, they retard markedly the course of the oxidation. Some years later with Leon[5] he noted that the presence of moisture does not modify the speed of the reaction and that an appreciable quantity of carbon dioxide is formed. Leon and Lister[6] studied the effect of the gradual purification of the rubber on the speed of oxidation and noted similarly the protective influence of a supplementary addition of the resins obtained by acetone extraction of the rubber and the remarkable behavior of dried latex films.

Meantime, Gorter[7] examining the phenomenon of tackiness, carried out experiments similar to those of Peachey, but at 25° C. His experimental results show that the speed of oxidation, which is very low during the first days, is progressively accelerated, reaches a maximum towards the thirtieth day, and then rapidly diminishes. In the case of balata, Dawson and Porritt[8] observed the autocatalytic nature of the reaction.

In an important study of the products of oxidation of rubber and of guttapercha, Kemp, Bishop, and Lasselle[9] have given curves, representing the percentage gain in weight as a function of the time of oxidation at 25° C for raw crepe and crepe that has undergone various extractions, as well as carefully purified crepe; in any case a test on the raw crepe proceeded only as far as a very low degree of oxidation.

To continue, mention may be made that, among the papers by Farmer and his collaborators, were experiments on 2 per cent benzene solutions which bring out the very pronounced effect of very small quantities of oxygen on the diminution of the molecular weight[10]; the work of Carpenter[11] on the influence of oxygen pressure, which showed that, at least at the beginning of oxidation, the speed of absorption of oxygen at 40° C by smoked sheet increases with pressure[12], and the conclusions of Bolland and Gee[13] in the mechanism of the oxidation of simple nonconjugated olefins, based principally on experiments with ethyl linoleate.

As regards the effect of substances able to act on oxidizability in minute quantities, this has been clearly revealed in general terms by Moureu and Dufraisse[14]. Nevertheless, in the case of raw rubber although numerous workers have pointed out the protection exerted by the natural antioxidants[15], one finds few results on the action of other substances. Leon and Lister[6] observed that dinitrobenzene and hydroquinone retard definitely the oxidation of natural rubber crepe, and in the opposite direction the experiments of Williams and Neal[16] show that impregnation of raw rubber by a proöxidant, such as copper stearate, leads to a disappearance of the induction period. Finally, Blake and Bruce[17], studying the effect of light on raw rubber, point out that products which act as antioxidants on vulcanized rubber actually accelerate the development of tackiness.

Thus it will be seen that knowledge of the kinetics of the oxidation of raw

rubber comes primarily from fragmentary experiments, and it seemed interesting, within the framework of a wider investigation, to endeavor to clarify by systematic experiments the influence of various factors on the course of the phenomenon.

## EXPERIMENTAL TECHNIQUE

In this investigation, a method has been used with which it is possible to determine, with maximum precision and sensitivity, the quantity of oxygen entering into the reaction. Gravimetric measurements are less sensitive and less practicable than volumetric measurements; further, the liberation of gas or volatile products during the course of the reaction may, beyond a certain level of oxidation, falsify the results enormously[18].

Nor does the manometric method avoid this criticism. In the Dufraisse apparatus[19] this cause of error is partially eliminated because the humidity and the other condensable substances act only by their vapor pressure at ordinary temperatures, but there remain, nevertheless, the uncondensable gases. We have to note that, because of its construction, the apparatus makes possible, at any desired moment, a new sweeping by means of oxygen; the test therefore starts again in an atmosphere free of foreign gases. In general terms, the accumulation of these gases in a confined atmosphere invalidates the measurement of real speed of oxidation and, by lowering the partial pressure of oxidation, acts on the conditions of reaction without mentioning the final inhibiting effect that certain of these products may show.

It was, nevertheless, decided in favor of a manometric method in view of the convenience of being able to introduce into the reaction vessel traps capable of absorbing the gases and volatile products, *viz.*, fragments of caustic potash and a little tube containing pumice stone soaked with sulfuric acid. The procedure is not perfect because, in spite of these precautions, there remains at the conclusion of an experiment some gaseous residue other than carbon dioxide and oxygen. This residue, although not negligible[20], is small and should not really affect the rate of the phenomenon. It should be pointed out that Mesrobian and Tobolsky[21] have recently described an arrangement involving circulation which makes possible the absorption of gases evolved during the course of the oxidation. It is similarly indispensable to be able to work under constant oxygen pressure. Although arrangements conforming to this condition had already been used by various authors[22], some did not maintain a constant temperature and others were too complicated to allow easily a number of simultaneous measurements. Therefore special equipment was designed permitting: (1) automatic maintenance of pressure in the oxidation vessel; (2) volumetric measurement of the quantity of oxygen consumed; (3) maximum reduction of the internal volume to increase the sensitivity; (4) total immersion in a thermostatic system to increase the precision of the measurements; (5) easy reproduction of unit in sufficient number to make possible simultaneous measurements.

## DESCRIPTION OF APPARATUS

Only the principle of the design and a summary description will be given here; complete details will be published subsequently on the construction and operation of the apparatus.

The oxygen required for the oxidation is prepared during the course of the absorption as required, within the apparatus itself, by electrolysis of a saturated solution of copper sulfate between a mercury cathode and an anode of platinum at a potential of about 6 volts. Under these conditions the copper dissolves in

the cathode, giving an amalgam, while the oxygen is evolved at the anode (no hydrogen is liberated from the secondary electrolysis of the sulfuric acid formed as long as the solution of copper sulfate remains sufficiently concentrated).

The reaction vessel can vary in form according to the physical condition of the material to be studied. With vulcanized rubber it is a simple cylindrical bulb, which may contain 10 grams of the sample, cut into small pieces. With raw rubber, the latter becomes viscous during the course of the oxidation, so there is placed in the interior of the bulb VR a pile of little shallow glass cups, on each of which is placed about 0.2 gram of rubber so that the surface of contact with the oxygen does not vary to too great an extent (Figure 1). At the

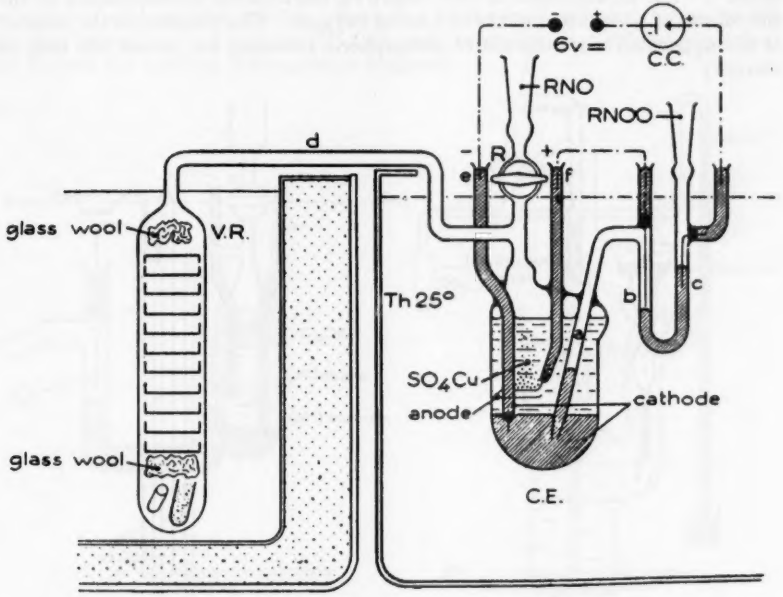


FIG. 1.—Scheme for the apparatus for oxidation at constant pressure. V.R., reaction vessel for experiments on crude rubber; C.E., electrolytic cell.

bottom of the bulb is placed a fragment of potash, and a small tube of pumice-stone soaked with sulfuric acid. For the investigation of solutions or liquids, it is necessary to arrange for stirring and for the condensation of solvent vapors; there is then used a vessel of the form indicated in Figure 2, stirring being brought about by the vertical to-and-fro movement of a glass device motivated by a solenoid. The reaction vessel is immersed in a bath of oil at a temperature that can be adjusted as required; in the experiments reported in this paper this temperature was maintained at 80° ± 0.1° C.

The electrolytic cell CE is connected to the reaction vessel by the tube *d*, the volume of which is as small as possible; this tube actually passes over the edges of the two thermostats in which the two portions of the apparatus are immersed; the electrolytic cell is immersed during the course of the experiments in a bath of water maintained at 25° ± 0.1° C. This cell is fitted with a stop-cock

R and a standard grinding RN.O. by which the various operations of filling or emptying are carried out. Three glass tubes enter the walls of the cell; two of these *e* and *f* carry the current to the electrodes, the third *a*, open at the lower end, enters the mercury of the cell, and is connected by a small contact manometer.

This manometer brings about automatic function of the electrolytic cell. When the pressure in the reaction vessel is lowered by absorption of oxygen, the mercury descends in the tube *a* and rises in branch *b* of the manometer; contact is then made between mercury and the platinum point *g* and closes the circuit of the cell, resulting in evolution of oxygen until the increase in pressure in the interior of the apparatus again causes the contact in the manometer to break[23]. The arrangement is very sensitive, the interval corresponding to the the release of a few hundredths of a cc. of oxygen. The pressure in the interior of the apparatus is a little above atmospheric pressure, *i.e.*, about 800 mm. of mercury.

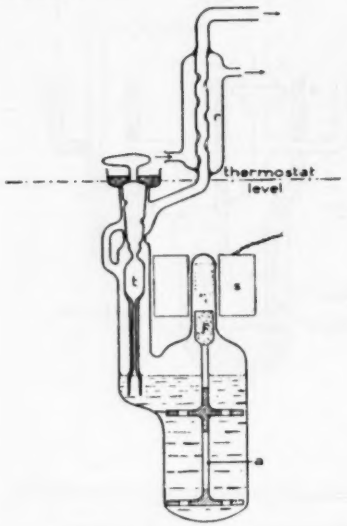


FIG. 2.—Apparatus used for measuring the oxidation of solutions.

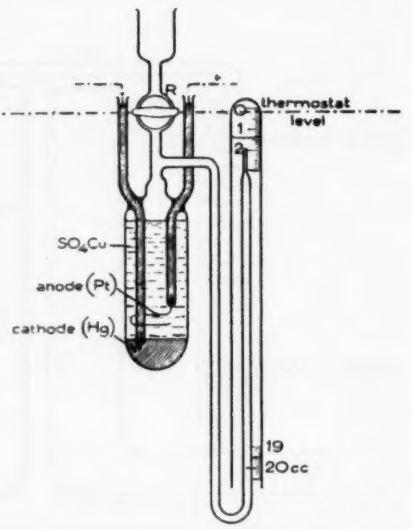


FIG. 3.—Control cell for measuring the oxygen consumed.

The calibration system consists of a second electrolytic cell (Figure 3) in series in the circuit and which, instead of discharging into the reaction vessel, accumulates the oxygen liberated in a graduated tube (graduated in 10th of cc.) and which is inverted in the water in the thermostat tank. The divergence between the quantities of oxygen liberated by several cells in series in the same circuit does not exceed 1 or 2 per cent. One can read every hour the volume of the oxygen to determine directly the average hourly speed of oxidation. It should be noted that measurement of the oxygen coming into the system can also be made with the aid of a meter which measures the quantity of current. Finally it should be pointed out, without going into details, that an automatic recording device is made desirable by the length of the experiments, which must sometimes go on for more than 300 hours. The principle is to record the

time $T$ which is necessary to absorb a quantity $Q$ of oxygen. This quantity $Q$ is determined in the following way: the arrangement of the manometer (Figure 4) is modified so that the making of the contact at $g$ starts the electrolytic cell functioning, and the latter feeds oxygen until another contact is made at $l$; the position of these points $g$ and $l$ is adjusted so that the quantity $Q^{24}$ will be liberated in a relatively short time (30 seconds to 1 minute); the time that elapses between the moment of contact at $l$ and that of a new contact at $g$ corresponds to the absorption of quantity $Q$. The recording device marks the time at which these contacts are made, thus giving a direct measure of the average speed of oxidation for the period under consideration.

After introducing the rubber into the reaction vessel the latter is fused on to the tube $d$. Then there is introduced by R first of all mercury and then a saturated solution of pure copper sulfate. Branch $c$ of the manometer is provisionally blocked by means of a stopper RN.OO, and the system is carefully evacuated by R until the solution is completely degassed.

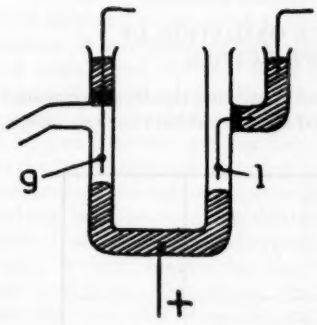


FIG. 4.—Manometer for automatic recording.

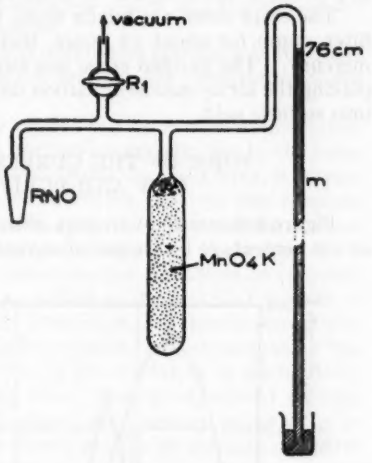


FIG. 5.—Arrangement for oxygen filling of the apparatus.

The apparatus is then placed in the thermostat and reattached by means of RN.O to a special tube system (Figure 5) carrying a mercury manometer and a bulb containing potassium permanganate. By $R_1$ the apparatus is evacuated by means of a water pump, then the permanganate bulb is heated to fill the apparatus with oxygen. Several successive operations are carried out before R is closed definitely, so as to eliminate the nitrogen of the atmosphere in the apparatus almost completely.

The stopper RN.OO is then withdrawn, and a little mercury is introduced into the contact manometer. The electrical connections are made, and measurements begin as soon as temperature equilibrium is attained, which requires about 10 minutes.

## RESULTS

Most of the tests have been carried out on first-quality pale crepe, which was used either in the raw state, or after purification, to determine the effect of the

natural antioxidants, and with or without additions of artificial antioxidants or deactivators. After a study of the experimental conditions and the factors influencing reproducibility, the influence of oxygen pressure and the concentration of rubber were examined. All the work was at 80° C; temperature is a factor that requires special study in view of the fact that it acts not only on the speed of the reactions, but also, by modifying the stability of certain peroxidic radicals, even on the direction taken by these reactions.

## PURIFICATION OF CREPE RUBBER

The crepe was sheeted thin by passing two or three times through the rolls of a mill without friction. This sheet, rolled in spun-glass fabric, was then extracted with acetone in a Soxhlet apparatus, cold and in darkness for 30 hours. It was next roughly dried *in vacuo* and again extracted (according to the method of Bloomfield and Farmer[25]) with a mixture of 48 parts of acetone and 52 parts of petroleum ether, at 25° C, in an atmosphere of nitrogen.

The crepe sheet was finally dried, first of all *in vacuo* obtained by means of a filter pump for about 12 hours, then at a reduced pressure of only 0.1 mm. mercury. The purified crepe was stored in a desiccator *in vacuo* after first displacing the air by means of carbon dioxide, obtained by projecting a little chalk into sulfuric acid.

## FORM OF THE CURVES FOR THE OXIDATION OF RAW AND PURIFIED CREPE RUBBER

Figure 6 shows the variation with time of the speed of oxidation (expressed as the percentage by weight of oxygen consumed by the rubber) for raw crepe,

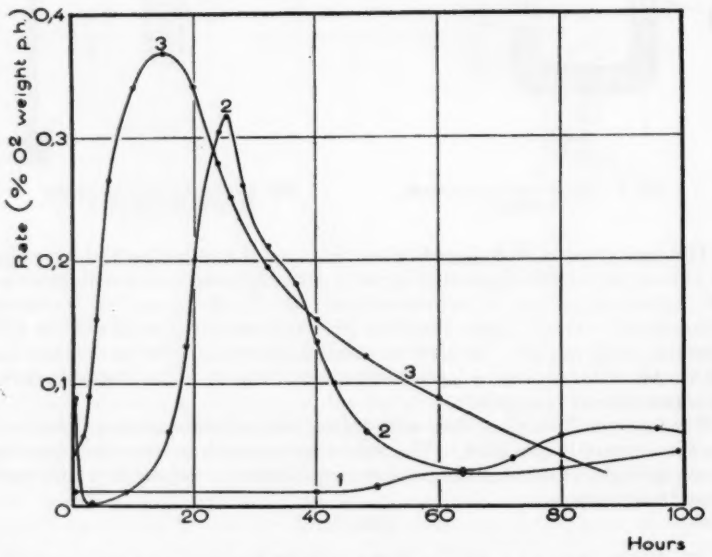


FIG. 6.—Rate of oxidation at 80° C as a function of the time: 1, natural crepe; 2, acetone-extracted crepe; 3, crepe treated by Bloomfield and Farmer method.

crepe purified by extraction with acetone for 30 hours, and crepe purified according to the method of Bloomfield and Farmer[25].

Obviously, the results obtained are the same as already observed by other workers on the influence of the natural antioxidants, but it should be noted that, whereas the curve for carefully purified crepe has a very regular form (with an initial phase during which the rate grows in an almost exponential fashion, reachès a maximum, and then falls away progressively according to logarithmic law), this is not the case for the other two materials. In particular, in the case of the crepe extracted only with acetone, the rate of oxidation, although initially fairly high, diminishes fairly quickly almost to the vanishing point: then it rises again rapidly in almost the same manner as for the purified crepe, but the descending part of the curve shows certain anomalies.

The initial phase of rate decrease, also noted by Horrobin, New, and Taylor[15], but in less definite form, is perhaps connected with the presence in the incompletely purified crepe of the "oxide" fraction mentioned by Bloomfield and Farmer[25]. The state of the present work does not afford any foundation for suggesting explanations for the other anomalies.

In any case, this emphasizes the inportant differences springing from causes that may appear to be slight, and the care necessary in the purification of the materials.

Further, if oxidation measurements are carried out on crepe samples taken from different parts of the same sheet and purified separately, but in the same manner, it is noticed that the curves of oxidation rates obtained have, it is true, the same form, but one finds considerable differences between the absolute values of the figures found. Thus, for example, systematic comparison of three samples has shown for the maximum of oxygen absorption, the values 0.42, 0.57, and 0.62 per cent per hour. These variations can doubtless be imputed to the heterogeneous nature of the rubber, as well as to the fact that in spite of the precaution taken to place the crepe on little cups, its distribution is not strictly homogeneous, particularly when it has melted, and consequently the rate of diffusion of the oxygen can intervene when oxidation is particularly rapid, without mentioning the "varnishing effect" due to superficial melting and oxidation. One should, therefore, not attach an excessive importance to the absolute value of results, and reference should always be made to a control which has undergone exactly the same treatment, except, of course, as regards the variable undergoing study.

## INFLUENCE OF STORAGE OF PURIFIED CREPE AT ROOM TEMPERATURE

It was necessary also to observe whether mere storage of the purified rubber for a certain time under the conditions already indicated would modifiy its oxidation characteristics. We therefore made three successive measurements at weekly intervals on crepe rubber submitted to the same operation of purification and preserved *in vacuo* in a desiccator. The results showed differences.

On the one hand, the values for the maximum were respectively 0.52, 0.56, and 0.61 per cent per hour, but this variation is not necessarily due to the time of storage, and may be attributed to causes similar to those indicated in the preceding paragraph. On the other hand, as shown on Figure 7, which represents the variations in the speed of oxidation as a function of the total percentage weight of oxygen absorbed, it is seen that, when the rate tends to be zero, the total quantity of oxygen absorbed seems to diminish regularly as a function

of the time of storage. This variation is important because this quantity, which is initially about 15 per cent, becomes after two weeks' storage only 8 or 9 per cent.

At the same time that the purified crepe was put into storage *in vacuo*, a portion of it was placed in a tube filled with air and fitted with a horizontal manometer. After two weeks at 25° C under these conditions, absorption of oxygen was still very small, and corresponded to about 2 mg. per 10 grams of

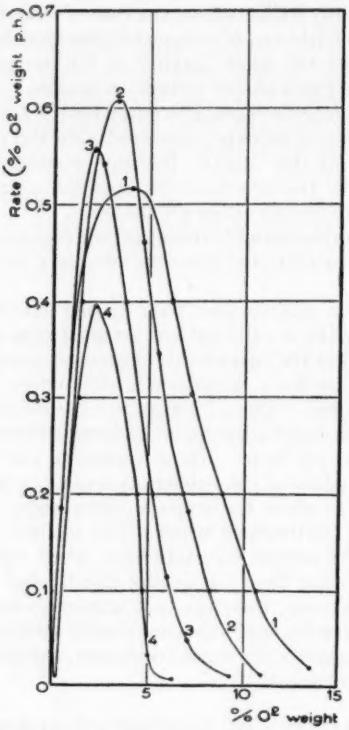


FIG. 7.—Influence of aging at ordinary temperatures on the oxidizability at 80° C of purified crepe: 1, immediately after purification; 2, after 8 days *in vacuo*; 3, after 15 days in vacuo; 4, after 15 days in air.

rubber. Nevertheless, if one then measures on this sample the rates of oxidation at 80° C, one notices two important changes (see curve 4 in Figure 7):

(1) In the initial phase, the rate decreases first of all and passes through a minimum, which is reached in about five hours; this should be compared with what happens in the case of an incompletely purified rubber.
(2) The total absorption of oxygen, at the moment when the rate becomes practically zero, is still less than that of the samples kept *in vacuo*.

It is certain that these observations demand further and more complete and detailed experiments before a well-based opinion can be offered as to the cause of these phenomena. But in any case, they confirm the fact that correct controls are indispensable.

## INFLUENCE OF THE PARTIAL PRESSURE OF OXYGEN

Four simultaneous measurements were made on purified crepe using, respectively:

(1) pure oxygen; (2) a mixture of equal volumes of nitrogen and oxygen; (3) air; (4) nitrogen containing about 3% of oxygen.

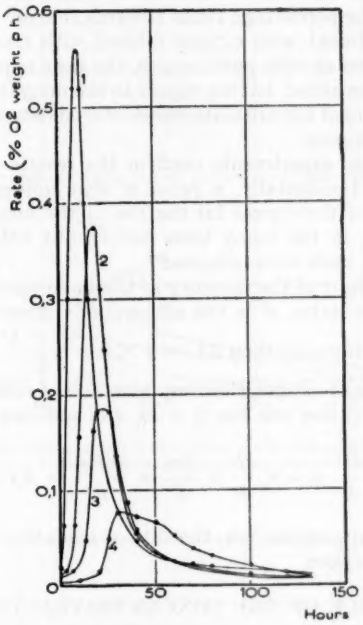


FIG. 8.—Influence of the partial pressure of the oxygen on the oxidizability at 80° C of purified crepe: 1, pure oxygen; 2, oxygen 50 and nitrogen 50; 3, air; 4, nitrogen containing about 3 per cent oxygen.

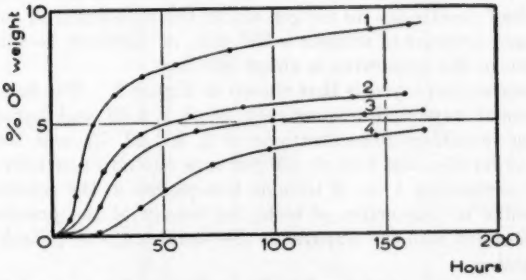


FIG. 9.—Variation of oxygen percentage absorption as a function of the time for different partial pressures of the oxygen: 1, 2, 3, 4 as Figure 8.

The results are shown in Figures 8 and 9. The first of these gives the variations in the speed of oxidation as a function of time; it will be observed that the oxygen pressure influences the results in two ways:

(1) The value of the rate maximum increases with the pressure, nevertheless without exact proportionality;
(2) the length of time taken to reach this maximum is longer for the lower oxygen pressures.

If one plots (Figure 9) the percentage of oxygen absorbed against the time, it is found that, after 150 hours, the time at which the rate of oxidation has become very slow, the percentage tends towards sharply different limits. If it is possible, in experiment with oxygen diluted with nitrogen, to arive at the same level of oxidation as with pure oxygen, the time required will thus be very long. It may even be asked, having regard to the magnitude of the divergences observed, if the nature of the ultimate stages of oxidation does not vary with the partial pressure of oxygen.

In any case, these experiments confirm the results of Carpenter[11] on the effect of pressure. Incidentally, a proof of that influence had already been found in the shape of the curves for the rise of the mercury in the Dufraisse manometer; in fact, in the many tests carried out with this apparatus, approximately straight lines were obtained[26].

When $h$ is the height of the mercury in the manometer tube; $s$ is the cross-sectional area of this tube; $P$ is the atmospheric pressure; $\Delta V$ is the actual volume absorbed in time $\Delta t$; then $\Delta V = s \times \Delta h \cdot \frac{P - h}{P}$.

Since the pressure of oxygen $Po_2$ is equal to $P - h$ and, further, as the curve obtained is a straight line one has $h = kt$, and one can write for the rate of oxidation:

$$\frac{dV}{dt} = s \times \frac{dh}{dt} \times \frac{Po_2}{P} = \frac{skPo_2}{P} = KPo_2$$

Thus, as a first approximation, the rate of oxidation is proportional to the partial pressure of oxygen.

## INFLUENCE OF THE CONCENTRATION OF RUBBER

It was also of interest, from the kinetic point of view, to examine how the rate of oxidation varied with changes in the concentration of rubber when the latter was diluted with a solvent. The solvent used was toluene after verifying that it absorbed practically no oxygen under the experimental conditions. At 80° C the vapor pressure of toluene is 300 mm. of mercury, so the partial pressure of oxygen in the apparatus is about 500 mm.

The apparatus employed is that shown in Figure 2. The tests were carried out on 2 grams of crepe and, respectively, 98, 6, 2, 0.66, and 0 grams of toluene, corresponding to rubber concentrations of 2, 25, 50, 75, and 100 per cent by weight. In order that the test at 100 per cent should be strictly comparative, a small bulb containing 1 cc. of toluene was placed in the reaction vessel. It was not possible in this series of tests, by reason of the presence of toluene vapor, to introduce into the apparatus the usual traps of potash and sulfuric-saturated pumice.

The results are indicated graphically in Figures 10, 11, and 12. Figure 10 gives the rates of absorption in hourly percentages as a function of time. It will be seen that the maximum rate is small and occurs later as the concentration of rubber in the solution is diminished. If the values for the maximum rate are plotted as a function of the concentration of rubber, it will be observed that there is very definite indication of proportionality.

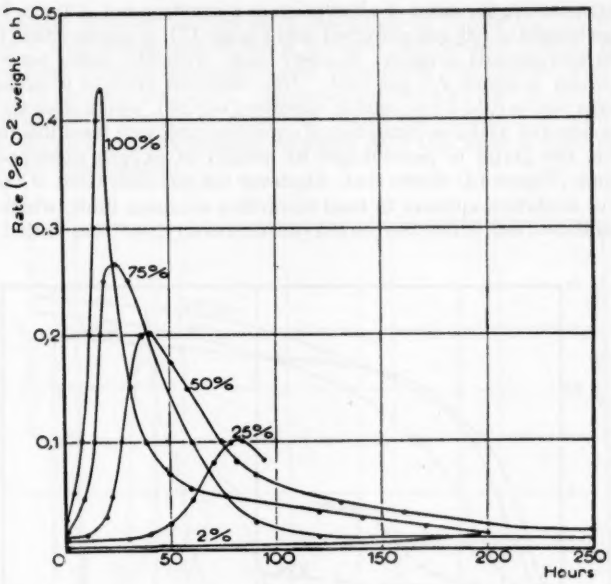


FIG. 10.—Influence of the concentration of the rubber on the oxidizability at 80° C. of purified crepe. Numbers on curves indicated the respective concentrations in toluene.

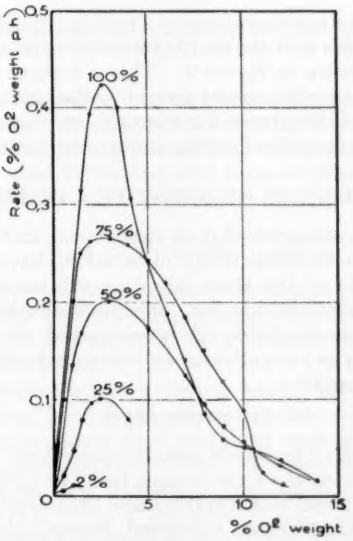


FIG. 11.—Variation of oxidizability as a function of percentage oxygen absorption, for various concentrations.

By representing the rates of absorption as a function not of time, but of the percentage weight of oxygen absorbed (see Figure 11), it appears that the maximum rate corresponds roughly, in every case, with the same percentage of oxygen, which is about 2.8 per cent. One observes definite irregularities on these curves above 8 to 9 per cent of absorbed oxygen, which irregularities are perhaps connected with the formation of oxidation products insoluble in toluene.

Finally, the graph of percentages by weight of oxygen absorbed plotted against time (Figure 12) shows that, whatever the concentration of the rubber, the level of oxidation appears to tend towards a common limit, which was not the case in those tests where the partial pressure of oxygen[27] was varied. It will

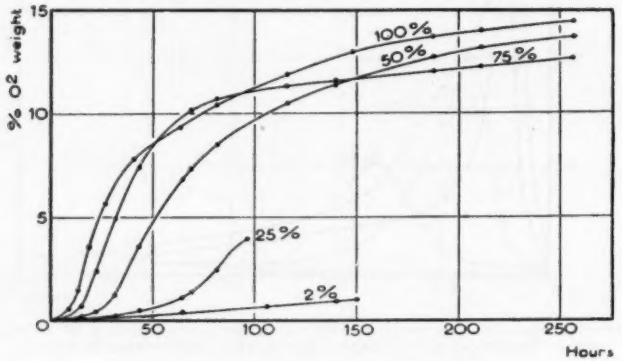


FIG. 12.—Variation of percentage oxygen absorption as a function of time for various concentrations.

be noted that the curve corresponding to a rubber concentration of 75 per cent seems abnormal and also that the limiting level of oxidation is here higher than for the experiments shown in Figure 9. This is a point that must be clarified later, particularly because the results given by other authors, Leon and Lister[6], and Kemp and his collaborators[9], for example, on variously treated samples, show notable differences in the limiting levels of oxidation.

## INFLUENCE OF NEGATIVE CATALYSTS

The preliminary experiments that we shall report, and which constitute only a fraction of the more complete study undertaken, have a bearing on the influence on oxidizability of the three following substances: (1) A well known antioxidant for vulcanized rubber, *viz.*, phenyl-$\beta$-naphthylamine; (2) An antioxidant whose effect on vegetable oils is recognized, *viz.*, $\alpha$-tocopherol; (3) A compound functioning as a deactivator on vulcanized rubber, *viz.*, the zinc salt of mercaptobenzimidazole[28].

### PURIFIED CREPE

The crepe was purified by simple acetone extraction. The ingredients were incorporated by diffusion, the crepe sample being immersed in a benzene solution of the substance under consideration and then dried to constant wight *in vacuo*. The samples thus treated contained, respectively, about 5 per cent of the zinc salt of mercaptobenzimidazole and 10 per cent of the two other products. The control sample underwent a similar treatment in benzene only.

The results obtained are shown in the graph on Figure 13. It will be seen that phenyl-β-napthylamine shows a powerful antioxidant action, the rate of oxidation first diminishing rapidly and then being maintained at a very low level (0.0015 per cent per hour). The α-tocopherol also has the effect of slowing down considerably the rate of oxidation, which is about 0.02 per cent per hour, this rate showing anyhow a slight decrease with the lapse of time (within the limits of the experiments).

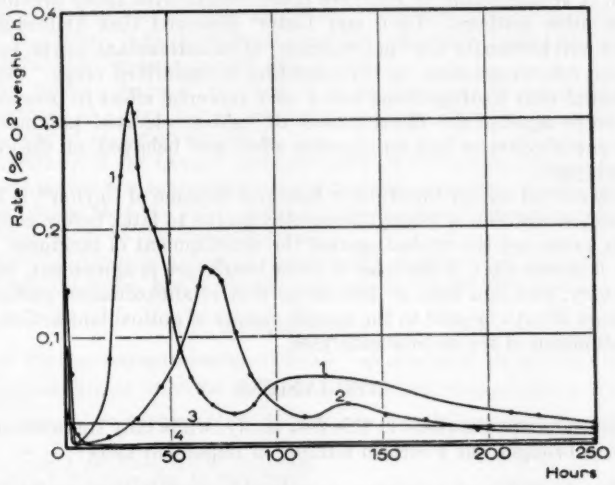


FIG. 13.—Influence of various substances on oxidizability at 80° C of acetone-extracted crepe: 1, control; 2, with 5% zinc mercaptobenzimidazolate; 3, with 10% α-tocopherol; 4, with 10% phenyl-β-naphthylamine.

In the case of the zinc salt of mercaptobenzimidazole, on the contrary, it is observed that the rate of oxidation varies according to a curve of form analogous to that for purified crepe, but the maximum is retarded and has a value of about one-half. Here one must be dealing with a mechanism different from that of antioxidants, and its study might well lead to interesting interpretations.

### RAW (UNPURIFIED) RUBBER

Circumstances have not yet permitted carrying out measurements of oxidation with the apparatus used for the preceding tests at constant oxygen pressure. Nevertheless, it seems useful to give some results obtained by the ordinary manometric method.

Milling into unpurified crepe on the one hand 2 per cent of phenyl-β-naphthylamine, on the other hand 2 per cent of the zinc salt of mercaptobenzimidazole, the oxygen absorptions were compared with those of the same crepe which had undergone identical mastication. It was noticed that the presence of phenyl-β-naphthylamine only retarded the oxidation of the crepe slightly (the absorption being about 5/7 that of the control), while the zinc salt of mercaptobenzimidazole diminishes this rate by about three times.

This shows, therefore, that an antioxidant like phenyl-β-naphthylamine has but little effect when used in addition to the natural antioxidants, while the

deactivator must combine its action with the natural antioxidants to give an improved protection.

Nevertheless, if similar tests are carried out with smoked sheet or dried latex, instead of with crepe, somewhat different results are obtained. Phenyl-β-naphthylamine reduces the rate of oxidation to about one-half, while the zinc salt of mercaptobenzimidazole has only a slight influence on the oxidizability. Perhaps the influence of certain nonrubber components would serve to explain these anomalies.

Again, it is interesting to compare these results with those previously obtained by other authors. Leon and Lister[6] observed that hydroquinone, a compound well known for the "polyvalence" of its antioxidant power, has a very pronounced retarding action on the oxidation of unpurified crepe. Blake and Bruce[17] found that hydroquinone had a very powerful effect in preserving unpurified crepe against the development of light-accelerated tackiness, while phenyl-β-naphthylamine had an opposite effect and behaved, on the contrary, like a proöxygen.

In tests carried out by the Rubber Research Scheme of Ceylon[29], it has been noted that the addition of phenyl-β-naphthylamine to latex before coagulation effectively protected the rubber against the development of tackiness.

Thus, it is seen that, while some of these results are in agreement, others are contradictory, and in a field as delicate as that of antioxidants, particular attention must always be paid to the specific nature of antioxidant action and the close relationship of the inverse catalyses.

## CONCLUSIONS

The experiments described in this first study, while only fragmentary, have nevertheless brought out a certain number of important facts:

(1) The possibility of obtaining reproducible quantitative results with rubber only when the experiments are performed simultaneously with identical samples.
(2) The great influence exercised on the phenomenon by the length of time the samples are kept[30].
(3) The part played on the oxidation characteristics by the partial pressure of oxygen and by the concentration of rubber.
(4) The existence of different limiting levels of oxidation according to the experimental conditions and the previous history of the samples.
(5) The differences in behavior towards raw rubber of antioxidants and deactivators.

Many problems are thus raised in this complex matter of the oxidation of rubber, its protection, and the mechanisms implied, and it is hoped that a deep study of these phenomena, facilitated by the use of the new equipment, will throw some light on the subject.

## SUMMARY

After a summary of the main works on the mechanism of rubber oxidation and the antioxidant effect, the principle of a method for the direct measurement and automatic recording of oxidation rates under constant pressure is given. The oxygen necessary for the reaction is produced inside the apparatus by the electrolysis of a solution of copper sulfate, and the noncondensable gases formed during the oxidation are absorbed by caustic potash and sulfuric acid-pumice.

Some results obtained with this apparatus during a systematic study of the oxidation of purified crepe at 80° C are described. The influence of the oxygen pressure of the concentration of rubber, of the effects resulting from the transformation undergone by purified crepe, and finally of the action of some antioxidants, were investigated.

Without discussing the theoretical interpretations, various experimental observations can be made.

(1) Even when using ordinary methods of conservation in high vacuum, the samples of rubber undergo modifications which alter its characteristics of oxidation; it is, therefore, necessary always to make simultaneous comparative measurements with a blank.

(2) The general shape of the rate of oxidation-time curves indicates the existence of a very strong maximum corresponding closely to the same amount of absorbed oxygen.

(3) Variations of the oxygen pressure react on the course of the oxidation.

(4) Variation of the concentration of rubber (observed on solutions in toluene) shows that the value of the maximum rate of oxidation is inversely proportional to the concentration.

(5) Phenyl-β-naphthylamine has practically no action on the oxidizability of natural crepe, but is a good antioxidant for purified crepe.

## REFERENCES


[1] Dufraisse, in "The Chemistry and Technology of Rubber," edited by Davis and Blake, New York, **1937**, p. 440.

[2] Le Bras, *Compt. rend.* **217**, 297 (1943); *Rev. gén. caoutchouc* **21**, 3 (1944); RUBBER CHEM. & TECHNOL. **20**, 949 (1947).

[3] Le Bras and Viger, *Rev. gén. caoutchouc* **21**, 89 (1944); RUBBER CHEM. & TECHNOL. **20**, 962 (1947). p. 440.

[4] Peachey, *J. Soc. Chem. Ind.* **31**, 1103(1912).

[5] Peachey and Leon, *J. Soc. Chem. Ind.* **37**, 55T (1918).

[6] Leon and Lister, *J. Soc. Chem. Ind.* **46**, 220T (1937).

[7] Gorter, *Caoutchouc & gutta-percha* **12**, 8724 (1915).

[8] Dawson and Porritt, *Trans. Inst. Rubber. Ind.* **2**, 345 (1927).

[9] Kemp, Bishop, and Lasselle, *Ind. Eng. Chem.* **23**, 1444 (1931).

[10] Farmer and Sundralingam, *J. Chem. Soc.* **1943**, p. 125.

[11] Carpenter and Twiss, *Nature* **154**, 673 (1944).

[12] Carpenter obtained a similar result for vulcanized rubber, which impairs the earlier conclusions of Williams and Neal (*Ind. Eng. Chem.* **22**, 874 (1930)) and Morgan and Naunton (*Proc. Rubber Tech. Conf.* London, **1938**, p. 527.

[13] Bolland and Gee, *Trans. Faraday Soc.* **42**, 236 (1946).

[14] Moureu and Dufraisse, *Compt. rend.* **177**, 204 (1932).

[15] Dufraisse and Drisch, *Rev. gén. caoutchouc* **8**, No. 75, 39 (1931); Horrobin, New, and Taylor, *Trans. Faraday Soc.* **42**, 252 (1946).

[16] Williams and Neal, *Ind. Eng. Chem.* **22**, 874 (1930).

[17] Blake and Bruce, *Proc. Rubber Tech. Conf.* London, **1938**, p. 736; *Ind. Eng. Chem.* **33**, 1198 (1941).

[18] Dufraisse and Le Bras, *Caoutchouc et Plastiques* **2**, 37 (1939).

[19] Dufraisse, RUBBER CHEM. & TECHNOL. **11**, 268 (1939); *Rev. gén. caoutchouc* **18**, 185 (1941).

[20] It is greater than the quantity of nitrogen which remains in the atmosphere inside the apparatus.

[21] Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 482 (1947).

[22] Kohman, *J. Phys. Chem.* **33**, 226 (1929); Morgan and Naunton, *Proc. Rubber Tech. Conf.* London, **1938**, p. 527; Milligan and Shaw, *Proc. Rubber Tech. Conf.* London, **1938**, p. 537; Van Amerongen, *Rev. gén. caoutchouc* **20**, 136 (1943); Carpenter and Twiss, *Nature* **154**, 673 (1944); Bolland, *Proc. Roy Soc.* **A186**, A18 (1946).

[23] Branch c of the manometer is, in principle, open to the outside air. If it is desired to eliminate with greater certainty the variations in atmospheric pressure, this end of the manometer can be connected to a control vessel immersed in the thermostat.

[24] This quantity is fixed approximately by a previous experiment according to the volume of mercury introduced into the manometer; it is arranged to be approximately 1 cc. The speed of oxidation can be considered as negligible in comparison with the speed of formation of oxygen.

[25] Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1940).

[26] Dufraisse and Le Bras, *Proc. Rubber Tech. Conf.* London, **1938**, p. 555.

[27] It will be noted, in comparing Figures 9 and 12, that the limiting level of oxygen absorption differs sharply for these two series of experiments, when working in pure oxygen. This is not surprising, for in addition to the differences that can be attributed to the toluene vapor and to variation in oxygen pressure, the tests shown in Figure 9 were carried out on pruified crepe as were those in Figure 12, but after a longer period of storage; from Figure 7 it is known that this period of storage has a very definite influence on the total percentage of oxygen absorbed.

[28] Le Bras and Hildenbrand, *Compt. rend.* **223**, 724 (1946).

[29] Rubber Research Scheme, "Report of the Work in 1944," p. 4.

[30] It will be shown in a subsequent paper that this factor also has a markedly modifying influence on the oxidation characteristics of rubber-sulfur vulcanizates.

# AGING OF GR-S VULCANIZATES. III. SOME EFFECTS OF OXYGEN AND TEMPERATURE ON AGING*

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## INTRODUCTION

Previous papers in this series[1] described the effects of various aging treatments on a GR-S tread mix accelerated with mercaptobenzothiazole (MBT)[2]. In the light of these results a larger investigation was undertaken, and an account of this up to May, 1945, has been given[3]. In addition to continuing this main investigation, experiments have since been made to examine the following aspects of the aging of GR-S; (1) effect of oxygen on changes in tensile properties, as shown by a comparison of prolonged vulcanization in a mold with air aging at the same temperature; (2) effect of high oxygen concentration, as in the oxygen bomb test, on tension set, the object being to confirm the tentative conclusion[4] that this leads to increased set; (3) effect of using a high temperature (80° C) in the oxygen bomb test; (4) effect of prolonged air aging at 100° C.

TABLE 1

| | A | C | D | E | F |
|---|---|---|---|---|---|
| GR-S (standard, as made in 1943–4) | 100 | 100 | 100 | 100 | 100 |
| EPC black | 50 | 50 | 50 | 50 | 50 |
| Zinc oxide | 3 | 3 | 3 | 3 | 3 |
| Stearic acid | 2 | 1 | 1 | 1 | 1 |
| Sulfur | 1.75 | 1.5 | 1.5 | 3.0 | 3.0 |
| Mercaptobenzothiazole (MBT) | 1.75 | 1.5 | — | 1.5 | — |
| Tetramethylthiuram disulfide (TMT) | — | — | 0.5 | — | 0.5 |
| Diphenylguanidine (DPG) | 0.1 | — | — | — | — |
| Pool aromatic extract, Group 4* | 7 | — | — | — | — |
| Pine tar | 3 | 3 | 3 | 3 | 3 |
| *Vulcanization* | | | | | |
| Temperature (° C) | 141 | 153 | 135 | 153 | 135 |
| Undervulcanization (min.) | 15; 30 | 20 | 15 | 12 | 10 |
| Optimum vulcanization (min.) | 60 | 60 | 45 | 35 | 30 |
| Overvulcanization (min.) | 180 | 180 | 135 | 105 | 90 |

* Byproduct of petroleum refining, comprising unsaturated and aromatic components; the "Group 4" material is of viscous tarry consistency.

The present report summarizes the results of these experiments and those more recent results from the main program, which show the effect of high oxygen concentration on the aging of GR-S vulcanizates.

## MIXINGS AND VULCANIZATION

Table 1 gives relevant particulars of the mixes discussed.

All specimens were cut from press-vulcanized sheets 0.1 inch thick.

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## EFFECT OF PRESENCE OF OXYGEN DURING AGING

The optimum vulcanizates of mixes C, D, E, and F were aged in air at their respective vulcanizing temperatures for periods equal to the difference between optimum and overvulcanization, as shown in Table 1. These aged samples had thus received the same heat treatment as the corresponding unaged overvulcanized samples; comparison of the data for these two sets of samples (Table 2)

TABLE 2

| Property | Mix | Optimum vulcanized, aged | Overvulcanized, unaged |
|---|---|---|---|
| Tension strength (lb./sq. in.) | C | 1620 | 2260 |
| | D | 1440 | 1780 |
| | E | 1000 | 2240 |
| | F | 1320 | 1760 |
| Breaking elongation (%) | C | 280 | 400 |
| | D | 300 | 350 |
| | E | 140 | 280 |
| | F | 200 | 240 |
| Modulus at 100% (lb./sq. in.) | C | 320 | 250 |
| | D | 275 | 240 |
| | E | 545 | 440 |
| | F | 435 | 420 |
| B.S. hardness number | C | 55 | 56 |
| | D | 56 | 58 |
| | E | 44 | 44 |
| | F | 41 | 41 |

therefore shows the effect of the presence of air during aging.

The following conclusions are indicated by these results:

(1) The presence of air always led to lower tensile strength and breaking elongation and higher modulus, *i.e.*, oxygen accelerated tensile deterioration and stiffening, as was found in similar experiments by Hunter[5]. The increased stiffening, however, is not reflected in the hardness figures.
(2) These effects of oxygen are always greater with the MBT mixes (C and E) than the TMT mixes (D and F), though this may be because the former were aged at a higher temperature (153° C as against 135° C).
(3) The effect of oxygen in promoting loss of tensile strength and elongation is greater when the GR-S is vulcanized with 3 per cent sulfur (mixes E and F) than when only 1.5 per cent is used (mixes C and D), but this difference is not shown by modulus.

## EFFECT OF HIGH OXYGEN CONCENTRATION ON STRESS-STRAIN PROPERTIES

Data have already been given only for 2- and 6-day oxygen-bomb aging periods, and the results showed no obvious difference from equal periods of 70° C air aging. However, as stated[4] 18-day bomb tests have since shown this test to be the more severe. The data for this aging period are given in Table 3, along with those for the same period in air at 70° C.

The increased oxygen concentration in the bomb test generally accelerated the fall in tensile strength. It also accentuated the loss of elongation and the increase in modulus of all except the undervulcanized samples of the high-sulfur mixes E and F; with these latter samples the high oxygen concentration exerted a softening effect.

It has already been pointed out that oxygen-bomb aging often causes the stress-strain curve to become straighter, *i.e.*, less concave to the stress axis (as compared with samples aged in air or inert gas) or even convex to this axis. Further evidence on this point has now become available, pointing to the following conclusions:

(1) Undervulcanized samples aged for 6 or 18 days in the oxygen bomb always give stress-strain curves less concave to the stress axis (or even convex in their upper part) than specimens aged at the same temperature (70° C) in air; this is found with mixes A, C, D, E, and F.
(2) With optimum and overvulcanized samples of mixes C, D, E, and F, there is no evident difference in shape of stress-strain curve between air- and bomb-aged specimens, although the tendency for bomb aging to give straighter or convex curves is seen in mix A. Results described below lead to a similar conclusion.

TABLE 3

COMPARSION OF AIR AND OXYGEN (BOMB) AGING AT 70° C

OB = oxygen bomb, 300 lb./sq. in. All properties are expressed as percentage of unaged value.

| | | Tensile strength | | Breaking elongation | | Modulus at 100% | |
|---|---|---|---|---|---|---|---|
| Aged 18 days in | | Air | OB | Air | OB | Air | OB |
| Mix C | U* | 119 | 75 | 70 | 66 | 185 | 225 |
| | P | 95 | 69 | 78 | 61 | 155 | 210 |
| | O | 94 | 72 | 92 | 73 | 130 | 160 |
| Mix D | U | 120 | 64 | 81 | 63 | 150 | 185 |
| | P | 85 | 80 | 70 | 68 | 160 | 200 |
| | O | 85 | 72 | 77 | 69 | 140 | 180 |
| Mix E | U | 69 | 72 | 42 | 58 | 215 | 185 |
| | P | 80 | 61 | 64 | 50 | 170 | 180 |
| | O | 75 | 59 | 72 | 50 | 140 | 175 |
| Mix F | U | 83 | 67 | 50 | 63 | 220 | 175 |
| | P | 80 | 63 | 64 | 52 | 160 | 195 |
| | O | 88 | 73 | 83 | 58 | 135 | 170 |

* U, P, O denote under-, optimum, and overvulcanization, respectively (see Table 1).

As already pointed out[4], straightening or convexity of the stress-strain curve suggests the occurrence of plastic flow, and hence a breakdown of the molecular structure. Thus again, as in the data of Table 3, the undervulcanized samples show a breaking down of molecular structure during high-pressure oxygen aging, in contrast to the stiffening which oxygen appears to promote in well vulcanized GR-S.

## EFFECT OF HIGH OXYGEN CONCENTRATION ON TENSION SET

Mixes C and D were used, and to minimize aftervulcanization effects during aging, the overvulcanized samples were chosen. Dumb-bell specimens were aged for 10 days at 70° C, some in air and some in oxygen at 300 lb. per sq. in. Set was then measured by stretching to 200 per cent elongation for 15 minutes, the set being measured after recovery periods of 5, 10, 30, and 60 minutes (see Table 4).

The bomb-aged specimens show more set than those aged in air. Since, however, set after constant elongation depends on the modulus, *i.e.*, on the force

required to produce the elongation, it is necessary to take into account any difference in modulus at 200 per cent elongation between air- and bomb-aged samples. The ratio of the moduli for bomb- and air-aged specimens is:

Mix C bomb/air ratio = 1.2
Mix D bomb/air ratio = 1.0

For mix C, therefore, a somewhat higher set might be expected in the bomb-aged specimen, but from data relating set after constant elongation with modulus it seems unlikely that this small difference in modulus could account for the observed set ratio of 1.52. With mix D the higher set of the bomb-aged specimen obviously cannot be ascribed to any difference in modulus.

TABLE 4

TENSION SET (Percentage)

| Recovery time (min.) | | 5 | 10 | 30 | 60 | Average ratio bomb/air |
|---|---|---|---|---|---|---|
| Mix C | Air | 4.9 | 4.8 | 3.6 | 3.4 | 1.52 |
| | Bomb | 7.7 | 6.1 | 5.7 | 5.6 | |
| Mix D | Air | 4.7 | 3.2 | 3.0 | 2.1 | 2.00 |
| | Bomb | 8.1 | 8.0 | 4.9 | 4.6 | |

Taking the results as a whole, therefore, this experiment confirms the previous conclusion that GR-S vulcanizates aged in a high concentration of oxygen have an increased tendency to retain deformation It is not possible to say whether this increase represents permanent deformation, *i.e.*, greater plastic flow, as tentatively suggested[4], or merely slower disappearance of temporary strain (as would arise from the introduction of oxygenated groups in the molecule, as pointed out by Farmer in the discussion of that paper). The fact that the bomb/air set ratio does not change with the period of recovery favors the latter explanation.

## OXYGEN BOMB AGING AT 80° C

In bomb tests at 80° C and 300 lb. per sq. in. Shelton and Winn[6] found that the stiffening of GR-S vulcanizates was less in oxygen than in nitrogen, contrary to the findings of most other workers that oxygen promotes age-stiffening[4]. It was suggested[4] that the conditions of Shelton and Winn's experiments with oxygen may have favored oxidative degradation, and hence softening, rather than the more usual stiffening due (presumably) to oxygen bridging. Experiments were therefore made to see whether evidence in support of this suggestion could be obtained.

Optimum vulcanizates of mixes C, D, and E (see Table 1) were aged for 3 days in oxygen at 300 lb. per sq. in. and 80° C. Results, expressed as percentage of the unaged values, are given in Table 5 in comparison with estimated values for 3 days in air at 80° C, these values [Column (*a*)] being the mean of results for the equivalent periods at 70° C (6.75 days) and 100° C (0.6 day); as the samples used for the bomb tests had previously had 6 months' natural aging, a correction for this, based on the 25° C aging results, has been applied to the Column (*a*) figures to give those in Column (*b*).

Generally the increased oxygen concentration in the bomb test led to greater loss of tensile strength, as would be expected, while the effect on elongation depends on whether the uncorrected or corrected air aging values are taken. It did not generally lead to a greater increase in modulus; indeed if the corrected

TABLE 5

COMPARISON OF OXYGEN BOMB AND AIR AGING AT 80° C

| | Mix | Bomb | Air* (a) | Air* (b) |
|---|---|---|---|---|
| Tensile strength | C | 88 | 96 | 95 |
| | D | 80 | (96) | (94) |
| | E | 86 | (86) | (83) |
| Breaking elongation | C | 82 | 85 | 78 |
| | D | 73 | 81 | 73 |
| | E | 70 | 74 | 68 |
| Modulus at 100% | C | 148 | 137 | 150 |
| | D | 143 | 142 | 157 |
| | E | 141 | 149 | 159 |

* Values in brackets are approximate because the 70° and 100° C data did not agree well.

air aging figures, Column (*b*), are accepted, there was less stiffening in high-pressure oxygen than in air, in accordance with Shelton and Winn's results, since confirmed by their experiments published subsequently[7] to the present investigation.

An alternative way of studying the data is to consider the ratio between the percentage increase in modulus and the percentage fall in tensile strength. Table 6 gives the mean values of this ratio for optimum vulcanizates of mixes C, D, and E.

The lower ratio for the 80° C bomb test shows that this has produced less stiffening, for a given loss of strength, than air aging. (It can be shown from the standard errors that while the three air-aging methods are statistically indistinguishable, the 80° C bomb ratio is significantly lower than the mean for these three.) There is, thus, further confirmation that using a high oxygen concentration at 80° C favors oxidative degradation more than do the tests in air.

The 25° C air test is not shown in Table 6 because the changes were small, and the values of the ratio consequently erratic. However, the results for the longest aging periods (100 and 320 days) support Table 6 in showing that the 80° C bomb test gives a lower ratio than air aging.

A conclusion of practical importance is that an oxygen bomb test at 80° C is not a reliable means of reproducing the effects of natural aging, since the relative extents of the two opposing effects of oxygen (degradation by chain scission, and stiffening by oxygen bridging) are not the same as in natural aging. Shelton and Winn[7] reach a similar conclusion, stated in more general terms, as to the limitations of aging tests when high temperatures and oxygen pressures are used, and further evidence on this point is provided below.

TABLE 6

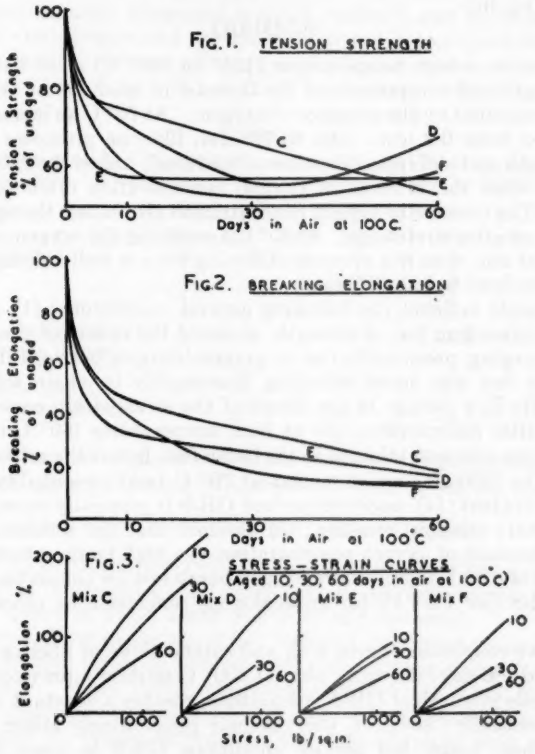
RATIO OF PERCENTAGE INCREASE IN MODULUS TO PERCENTAGE FALL IN TENSION STRENGTH

| Aging conditions | Mean ratio | Standard error of mean |
|---|---|---|
| 55° C in air | 5.2 | 0.8 |
| 70° C in air | 7.2 | 1.1 |
| 100° C in air | 7.0 | 1.1 |
| Mean of air results | 6.5 | 0.6 |
| Oxygen bomb at 70° C | 5.0 | 0.9 |
| Oxygen bomb at 80° C | 3.0 | 0.9 |

Reference has already been made[4] to the effect of oxidative degradation in making the stress-strain curve straighter or even upwardly curving, at least for undervulcanized samples. Except perhaps with mix C, the stress-strain curves of the 80° C bomb-aged sample did not show this effect, by comparison with 70° or 100° C air-aged samples. This confirms the observation that this effect of oxidative degradation is not marked in optimum vulcanizates.

## LONG-PERIOD AGING IN AIR AT 100° C

It has been pointed out[4] that in high-temperature air aging tensile strength appears to reach a constant value, or even to increase eventually, instead of




falling substantially to zero as is usual with natural rubber. To examine this point more fully, the 100° C air tests on optimum vulcanizates of mixes C-F were extended to 60 days. The complete aging curves are shown in Figures 1 and 2. Except for mix C, the tensile strength remained stationary beyond 30 days, or even increased, thus confirming the earlier observation. On the other hand, the elongation continued to fall, implying a continued stiffening, shown clearly by the stress-strain curves in Figure 3 for 10, 30, and 60-day aged specimens.

The following B.S. hardness numbers, expressed as percentage of unaged values, further show how greatly the rubbers have stiffened:

| Mix | C | D | E | F |
|---|---|---|---|---|
| Aged 60 days | 40 | 35 | 37 | 30 (46 after 30 days) |

The two mixes showing the final increase in tensile strength are those accelerated with TMT (D and F), which also show the greatest loss of extensibility and the greatest stiffening according to the hardness figures.

It thus appears that in uses involving prolonged subjection to heat, GR-S is more likely to fail by loss of extensibility than by loss of strength, since, even after 60 days at 100° C, all the four vulcanizates had tensile strengths of 1100–1300 lb. per sq. in.

## SUMMARY

Experiments at high temperatures (135° to 153° C) show that the fall in tensile strength and elongation and the increase in modulus of GR-S vulcanizates are accelerated by the presence of oxygen. At 70° C an increase of oxygen concentration from 0.2 atm. (air) to 20 atm. likewise promotes both loss of tensile strength and stiffening (increase of modulus), unless the rubber is undervulcanized, when the increase of oxygen concentration often results in less stiffening. The increase of oxygen concentration also causes the aged rubber to retain more set after stretching. At 80° C, increasing the oxygen concentration from 0.2 to 20 atm. does not promote stiffening even in well vulcanized rubbers, and may even lead to less stiffening.

These results indicate the following general conclusions: (1) oxidation, in addition to promoting loss of strength, is one of the causes of the stiffening of GR-S during aging, presumably due to oxygen-bridging between the molecules; (2) oxidation can also cause softening, presumably by chain scission, which further results in a change in the shape of the stress-strain curve and an increased set after deformation; (3) at high temperatures (80° C or above) increase of oxygen concentration, as in the bomb test, favors the softening reaction relative to the stiffening reaction, but at 70° C (and presumably below) this effect is not evident; (4) undervulcanized GR-S is especially susceptible to the softening (chain scission) reaction; (5) the fact that the softening reaction is favored by increase of oxygen concentration at a high temperature casts doubt on the value of a high-temperature oxygen bomb test for simulating the natural aging of GR-S (*see* Part IV for an analogous conclusion on other accelerated tests).

The above conclusions agree with and extend those of Shelton and Winn[10].

Prolonged (60-day) air-aging tests at 100° C confirm a previous suggestion[4] that the tensile strength of GR-S vulcanizates reaches a constant value or even increases eventually; however, they become progressively stiffer and less extensible. Thus, under hot service conditions GR-S is more likely to fail through inability to stretch than through loss of strength.

## REFERENCES

[1] Scott, *Trans. Inst. Rubber Ind.* **21**, 78 (1945); Fisher and Scott, *J. Rubber Research* **16**, 44 (1947).
[2] Mix A in the earlier work of Scott (*Trans. Inst. Rubber Ind.* **16**, 44 (1947)). The recipes for these earlier mixes should have included 3 parts of pine tar.
[3] Mixes C-F in the earlier work of Scott (*Trans. Inst. Rubber Ind.* **16**, 44 (1947)), which should have included 3 parts of pine tar.
[4] Scott, *Trans. Inst. Rubber Ind.* **16**, 44 (1947).
[5] Hunter, *India Rubber J.* **107**, 429 (1944).
[6] Shelton and Winn, *Ind. Eng. Chem.* **36**, 728 (1944).
[7] Shelton and Winn, *Ind. Eng. Chem.* **39**, 1133 (1947).

# IV. INFLUENCE OF THE VULCANIZING INGREDIENTS, ANTIOXIDANT, AND SOFTENER

## INTRODUCTION

This report deals with the influence of the following factors on aging in air at various temperatures and in the oxygen bomb (formulas are given in Table 1): (1) proportion of sulfur (mixes C and D, low; E and F, high); (2) choice of accelerator (mixes C and E, MBT; D and F, TMT); (3) use of a low proportion of sulfur supplemented by selenium (mix M); (4) vulcanization by TMT instead of sulfur (mixes J, K, L; to be compared with E, G, H); (5) removal of the antioxidant normally contained in GR-S (mixes G and K, to be compared with E and J; extra stearic acid was added in G and K to replace that removed by acetone-extraction); (6) use of a high proportion of softener of the petroleum aromatic extract type (mixes H and L, to be compared with E and J). The

TABLE 1

*Note.*—All mixes contain EPC black 50, zinc oxide 3, pine tar 3; variable ingredients are shown in the Table. Mixes C–F are the same as those show in Table 1 of Part III.

| Mix | C | D | E | F | G | H | J | K | L | M |
|---|---|---|---|---|---|---|---|---|---|---|
| GR-S | 100 | 100 | 100 | 100 | — | 75 | 100 | — | 75 | 100 |
| GR-S, acetone-extracted | — | — | — | — | 96 | — | — | 96 | — | — |
| Stearic acid | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 5 | 1 | 1 |
| Sulfur | 1.5 | 1.5 | 3 | 3 | 3 | 3 | — | — | — | 1 |
| Selenium | — | — | — | — | — | — | — | — | — | 3 |
| Mercaptobenzothiazole (MBT) | 1.5 | — | 1.5 | — | 1.5 | 1.5 | — | — | — | 1 |
| Tetramethylthiuram disulfide (TMT) | — | 0.5 | — | 0.5 | — | — | 3 | 3 | 3 | — |
| Diphenylguanidine (DPG) | — | — | — | — | — | — | — | — | — | 0.25 |
| Pool aromatic extract, Group 4 | — | — | — | — | — | 25 | — | — | 25 | — |

extracted GR-S used for mixes G and K was made by extracting the raw GR-S, sheeted and cut into small pieces, with acetone in a large Soxhlet apparatus for 24 hours.

## PROPERTIES OF THE UNAGED RUBBERS

As there were big differences between the rubbers before aging, which must be borne in mind in assessing their suitability in practical applications, these properties are shown in Table 2 and will be briefly discussed.

In the series C-F, reducing the sulfur retarded vulcanization and made the optimum vulcanizate softer and more extensible; tensile strength showed no consistent change. When sulfur was replaced entirely by TMT (mixes J, K, and L) the vulcanizate was still softer and more extensible, again without any consistent change in tensile strength; TMT vulcanization gave results less dependent on the vulcanizing time than sulfur vulcanization, as it does in natural rubber. Vulcanization with selenium plus sulfur (mix M) gave poor tensile strength and especially poor elongation, and the vulcanizate was relatively hard and stiff.

Change of accelerator from MBT (mixes C and E) to TMT (D and F) somewhat reduced tensile strength and (with the low proportion of sulfur) elongation also; modulus and hardness were little affected.

Removal of acetone-extractable material from the raw GR-S made the vulcanizate harder and slightly stiffer and less extensible (compare G and K with E and J). By contrast, the addition of softener had the reverse tendency (com-

TABLE 2

PROPERTIES OF UNAGED VULCANIZATES

| Mix. | C | D | E | F | G | H | J | K | L | M |
|---|---|---|---|---|---|---|---|---|---|---|
| *Vulcanization* | | | | | | | | | | |
| Temperature (° C) | 153 | 135 | 153 | 135 | 153 | 153 | 153 | 153 | 153 | 153 |
| Minutes[b] | 20 | 15 | 12 | 10 | 10 | 10 | 5 | — | 5 | 10 |
| | 60 | 45 | 35 | 30 | 30 | 30 | 15 | 15 | 15 | 30 |
| | 180 | 135 | 105 | 90 | 90 | — | 45 | — | — | 90 |
| Tension strength (lb./sq. in.) | 2020 | 1660 | 2060 | 1920 | 2160 | 1400 | 1900 | — | 1660 | 1920 |
| | 2480 | 1720 | 2120 | 1960 | 1580[a] | 2020 | 2040 | 2140 | 1640 | 1440 |
| | 2260 | 1780 | 2240 | 1760 | 1960 | — | 2000 | — | — | 1460 |
| Breaking elongation (%) | 670 | 590 | 500 | 680 | 550 | 600 | 670 | — | 670 | 420 |
| | 510 | 370 | 300 | 310 | 270[b] | 450 | 680 | 570 | 740 | 240 |
| | 400 | 350 | 280 | 240 | 240 | — | 640 | — | — | 210 |
| Modulus at 100% (lb./sq. in.) | 130 | 140 | 200 | 120 | 210 | 100 | 110 | — | 55 | 240 |
| | 190 | 210 | 380 | 330 | 395 | 225 | 105 | 170 | 55 | 370 |
| | 250 | 240 | 440 | 420 | 450 | — | 115 | — | — | 455 |
| B.S. hardness number | 79 | 81 | 71 | 92 | 61 | 79 | 73 | — | 103 | 53 |
| | 63 | 58 | 49 | 46 | 41 | 50 | 71 | 55 | 93 | 40 |
| | 56 | 58 | 44 | 41 | 37 | — | 70 | — | — | 38 |

[a] These results appear abnormally low, but no obvious cause could be found.
[b] The middle one of the three times represents the optimum; all samples were press-vulcanized as sheets 0.1 inch thick.

pare H and L with E and J). In the TMT-vulcanized mix, indeed, it gave a very soft stretchy vulcanizate with poor tensile strength; this is in keeping with the observation[1] that Naftolen R100, a material broadly similar to the petroleum aromatic extracts, seriously intereferes with vulcanization by TMT.

In determining the optimum vulcanization, measurements of tension set were made, but, as the elongation was varied from mix to mix, the results do not directly show the effect of the variations in composition. Allowing, so far as is possible, for these differences in conditions, none of the variations in composition appears to have markedly affected the set.

## AGING PROPERTIES

Tensile and hardness tests were made after the following aging treatments:

(1) air at 25° C: 32 and 100 days; 320 days (C-F only).
(2) air at 55° C: 10, 30, and 100 days; 300 days (C-F only).
(3) air at 70° C: 4, 12, 40, 120 days; 2 and 6 days (G-M only).
(4) air at 100° C: 1, 3, 10, 30 days.
(5) oxygen bomb at 70° C and 300 lb. per sq. in.: 2 and 6 days; 18 days (C-F only).

As the amount of numerical data from these tests is extremely large, only selected results and general conclusions will be presented. All aged values are expressed as percentage of the corresponding values for the unaged rubber.

### COURSE OF AGING CHANGES

To illustrate the general course of the aging changes, the 70° C air aging curves for optimum vulcanizates are given in Figures 1 and 2 (hardness data for C-F are incomplete because tests were not made after the shorter aging periods). To enable the wide range of aging periods to be plotted conveniently, a contracting time scale is used (abscissa proportional to $\sqrt{\text{time}}$; this is preferable to a logarithmic scale because zero time can be shown). The fact that the

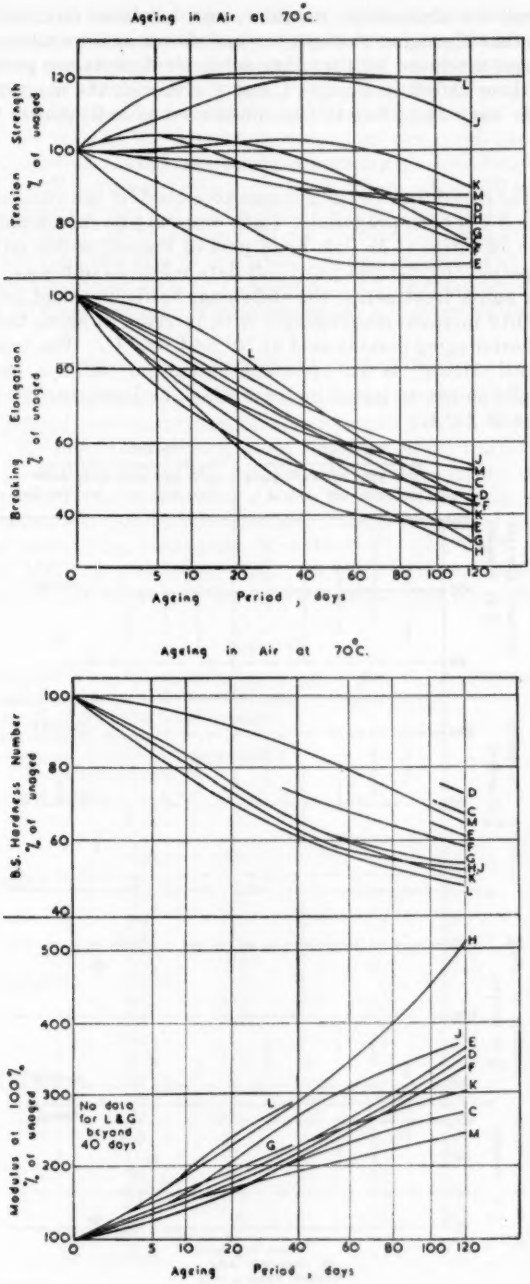

Ageing in Air at 70°C.
Tension Strength % of unaged
Breaking Elongation % of unaged
Ageing Period, days
Ageing in Air at 70°C.
B.S. Hardness Number % of unaged
Modulus at 100% % of unaged
No data for L & G beyond 40 days
Ageing Period, days

FIG. 2

curves, at least for elongation, modulus, and hardness number, are roughly linear means that the aging changes become slower as time advances.

The changes produced by the other aging treatments are generally similar in nature to those shown in Figures 1 and 2, although the magnitude and rate of the changes vary according to the conditions, as indicated in the following section.

## EXTENT OF AGING CHANGES

To show the magnitude of the changes produced by the various aging treatments, Figure 3 has been prepared. Each vertical line represents the range of values for the 10 mixes C-M (left-hand part of Figure) or for mixes C-F aged for a longer period (right-hand part); all data relate to optimum vulcanizates.

In the air aging treatments, the stiffening, hardening, and loss of strength and extensibility increase progressively with increase of aging temperature, in spite of the shorter aging periods used at 70° and 100° C. The tension strength graph for "All Mixes" is an apparent exception, perhaps because tensile strength usually shows an initial increase which had not reached its maximum after 100 days at 25° C.

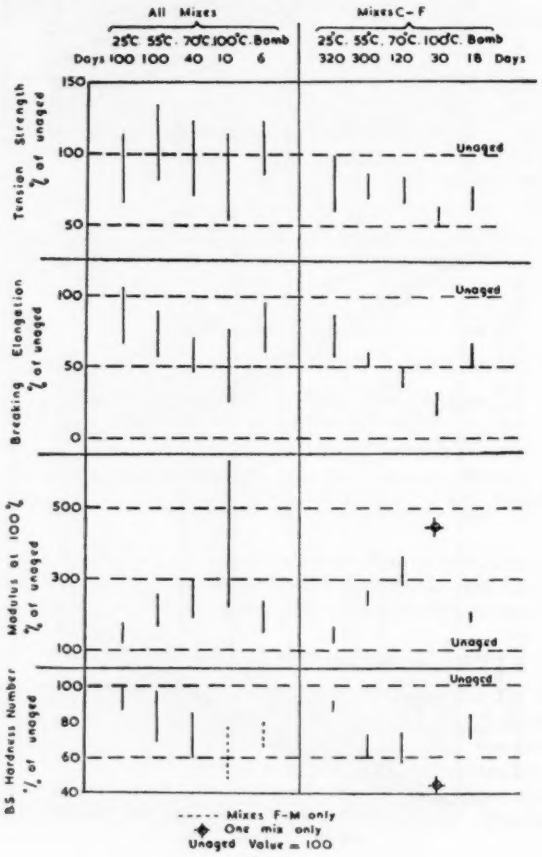

All Mixes
Mixes C–F
25°C. 55°C. 70°C. 100°C. Bomb
Days 100 100 40 10 6
25°C. 55°C. 70°C. 100°C. Bomb
320 300 120 30 18 Days
Tension Strength % of unaged
Breaking Elongation % of unaged
Modulus at 100% % of unaged
BS Hardness Number % of unaged
Unaged
----- Mixes F–M only
◆ One mix only
Unaged Value = 100

FIG. 3

The graphs for mixes C-F suggest that the oxygen bomb is, by comparison with air aging, more severe on tensile strength than on elongation, modulus, and hardness, which means that the increased oxygen concentration altered the relation between the changes in different properties, as indeed is not unexpected in view of the results already described[2] and those of Shelton and Winn[3].

The 25° C air test, as the nearest to normal service conditions, is perhaps the most significant on that account. It is, therefore, interesting to note from Figure 3 that a GR-S vulcanizate can be made which, after 320 days at 25° C (equivalent to nearly 2 years at the "normal" temperature of 15° C), shows no loss of tensile strength, or only about 10 per cent loss of extensibility, or only about 15–20 per cent increase in modulus, whether measured at 100 per cent extension or by a hardness test, *i.e.*, a change in B.S. hardness number from 63 to 57, though all these optimum aging results are not given by the same mix.

### EFFECT OF VARIATION IN COMPOSITION

The effects of changes in composition on the aging of well vulcanized samples (optimum or beyond) are summarized qualitatively in Table 3, the changes considered being: (1) low sulfur: change from 3 percent sulfur (mixes E and F) to 1.5 per cent (C and D); (2) TMT vulcanization: replacement of sulfur and accelerator by TMT (*i.e.*, comparing J with C-F; K with G; L with H); (3) selenium vulcanization: use of selenium and a small amount of sulfur in place of the normal sulfur (*i.e.*, comparing M with C-F); (4) TMT acceleration; replacement of MBT (C and E) by TMT (D and F); (5) extraction: removal of the antioxidant and other acetone-soluble components from the raw GR-S

TABLE 3

++ denotes a definite improvement in aging properties, *i.e.*, smaller losses of tensile strength and elongation, and less stiffening and hardening.
+ denotes a small or doubtful improvement.
O denotes no definite effect.
− denotes a small or doubtful adverse effect.
−− denotes a definite adverse effect.
O.B. denotes oxygen bomb.

| | Aging | Low sulfur | TMT vulc'n. | Selenium vulc'n. | TMT accel'n. | Extraction | Softener |
|---|---|---|---|---|---|---|---|
| Tensile strength | 25° C | + | + | + | − | O | + |
| | 55° | ++ | ++ | ++ | − | O | ++ |
| | 70° | ++ | ++ | + | O | O | ++ |
| | 100° | ++ | ++ | ++ | O | − | ++ |
| | O.B. | ++ | ++ | ++ | ++ | O | ++ |
| Breaking elongation | 25° C | ++ | ++ | + | − | + | + |
| | 55° | ++ | ++ | ++ | − | + | + |
| | 70° | ++ | ++ | O | O | − | O |
| | 100° | + | ++ | + | O | O | O |
| | O.B. | ++ | + | O | O | O | O |
| Modulus at 100% | 25° C | − | −− | − | −− | + | − |
| | 55° | O | − | ++ | − | O | O |
| | 70° | O | O | + | O | + | − |
| | 100° | O | ++ | ++ | O | O | −− |
| | O.B. | O | O | O | O | O | − |
| Hardness | 25° C | + | O | O | − | − | O |
| | 55° | ++ | − | O | − | − | O |
| | 70° | + | − | O | O | − | − |
| | 100° | [a] | + | ++ | [a] | O | −− |
| | O.B. | ++ | − | O | − | + | O |

[a] No results available.

(*i.e.*, comparing G with E, and K with J); (6) softener: replacement of 25 per cent of the GR-S by petroleum aromatic extract (*i.e.*, comparing H with E, and L with J).

The effects of these variables will be discussed separately:

(1) *Low Sulfur.*—This gives better maintenance of tensile strength and elongation under all the aging conditions examined. Apart from a doubtful indication of increased stiffening in the 25° C aging, the modulus changes appear to be unaffected, but there is always less hardening with the low proportion of sulfur.

(2) *TMT vulcanization*: As might be expected, this resembles and, in fact, usually surpasses the "low sulfur" in improving maintenance of tensile strength and elongation. On the other hand, the hardening and stiffening caused by aging are on the whole somewhat aggravated, except in the 100° C test, which thus appears misleading as an indication of behavior at lower temperatures. As the unaged TMT-vulcanized mixes are relatively soft (see J, K, and L in Table 2), this increased stiffening during aging may not be a very real disadvantage.

(3) *Selenium vulcanization.*—Low sulfur supplemented by selenium again generally helped to maintain tensile strength and elongation; its effects on the modulus and hardness changes were variable, but favorable on the whole. Compared with TMT vulcanization, selenium vulcanization resulted in greater loss of strength and elongation, especially at 70° and 100° C, and since it was inferior in strength and elongation even before aging, the TMT vulcanization clearly has the advantage when these properties are important. On the other hand, the selenium vulcanizates showed less stiffening and hardening in all the aging conditions, thus tending to reduce the big initial (unaged) difference between selenium and TMT vulcanizates in modulus and hardness.

(4) *TMT Acceleration.*—Substitution of TMT for MBT, without changing the proportion of sulfur, generally did not improve aging, indeed the deterioration, particularly at 25° and 55° C, was often greater. The exception was tensile strength in the oxygen bomb, which suggests that this test can give misleading indications as to the effects of air aging. The present results strengthen the conclusion[4] that a nonpersistent or flat-vulcanizing accelerator such as TMT is not in itself superior, as regards aging characteristics, to a persistent accelerator, such as MBT.

(5) *Extraction.*)—The effects of this treatment are much less serious than might have been expected, since it presumably removes the antioxidant. Unfortunately the unaged optimum vulcanizate of mix G gave an abnormally low tensile strength (see Table 2), so the degree of deterioration produced by aging is in some doubt. However, there still remain the results for mix K, and from the data as a whole there is little evidence of increased tensile deterioration as a result of acetone-extracting the raw GR-S. The effects on the modulus and hardness changes seem to be in opposite directions, but are in no case large. Assuming that the antioxidant was removed by the extraction, these results are directly contrary to those of Shelton and Winn[5], who found that antioxidant-free GR-S deteriorated very quickly in either air or oxygen.

(6) *Softener.*—Addition of a high proportion of petroleum aromatic extract improved the maintenance of tension strength under all aging conditions; improvement in the maintenance of elongation was less marked,

owing to the tendency of the softener to promote stiffening and hardening.

### CHOICE OF FORMULAS

In Table 4 the mixes (excluding G and K, which are not of practical interest) are arranged in order of merit according to their average behavior in the five aging conditions examined. A separate order is given for each property, because the mixes that maintain, say, tensile strength most satisfactorily do not necessarily show the least stiffening or hardening. This Table will help in selecting a mix formula to give the best maintenance of any particular property or combination of properties during aging.

TABLE 4

In each column the best mix is at the top

| Tensile strength | Breaking elongation | Modulus | Hardness |
|---|---|---|---|
| J, L | L | M | C |
| M | J | C | D |
| H | C, M | E, F | M |
| C, D | D | D | — |
| — | H | L, J | F, H, L |
| E, F | E, F | H | J |

## SUMMARY

The results of air aging at temperatures from 25° to 100° C and of oxygen-bomb aging are discussed in relation to the composition of the mix; notes are given also on the relation of composition to the properties before aging.

The main conclusions are: (1) a low proportion of sulfur or (still better) vulcanization by tetramethylthiuram disulfide (TMT) improves the maintenance of tensile strength and elongation under all conditions examined; a low-sulfur mix containing selenium gives results intermediate between the normal low-sulfur and TMT-vulcanized mixes; (2) when judged by the stiffening and hardening during aging, the relative merits of these alternative vulcanizing agents are different, age-stiffening being generally least with low sulfur plus selenium and greatest with TMT vulcanization; (3) on the whole, mercaptobenzothiazole (MBT) gave better results than TMT as an accelerator in mixes with the same proportion of sulfur; (4) acetone extraction of raw GR-S did not lead to the bad aging expected from the removal of antioxidant, but this point needs further study in view of contrary conclusions by other workers; (5) a large proportion of softener somewhat improves maintenance of strength but increases age-stiffening; (6) in general the formulation giving the best maintenance of tension strength and elongation does not give the least age-stiffening, and *vice-versa*; for the former, TMT vulcanization (possibly plus softener) appears best; for the latter an MBT-accelerated low-sulfur mix, possibly plus selenium, and (7) the 100° C air and the oxygen-bomb aging tests may give misleading indications of aging behavior in air at lower temperatures.

## REFERENCES

[1] Griffin, Newton and Scott, *J. Rubber Research* **16**, 1 (1947).
[2] Scott, *J. Rubber Research* **18**, 117 (1949); preceding article in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[3] Shelton and Winn, *Ind. Eng. Chem.* **36**, 728 (1944); **39**, 1133 (1947).
[4] Scott, *Trans. Inst. Rubber Ind.* **21**, 78 (1945).
[5] Shelton and Winn, *Ind. Eng. Chem.* **36**, 728 (1944).

# SOME OBSERVATIONS ON THE OXIDATION OF RUBBER IN LIGHT *

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## INTRODUCTION AND CONCLUSIONS

The work described in this paper is part of a larger investigation undertaken to find better means than those known at present of protecting rubber against the destructive action of light. It has been known for a long time that the protection of non-black mixings against light is far more difficult than protection against heat, and, in fact, the effect of light is such that the usual antioxidants, which normally retard the absorption of oxygen in the dark, fail to retard the oxygen intake under the action of light.

Most of the work undertaken in the past has been done with sources of light, often of ultraviolet light, giving a very high acceleration of the dark reaction. It was thought to be more interesting to use a relatively weak light source which would promote a rate of oxygen-absorption of the same order as the dark thermal reaction itself. Although it was thought possible, under such circumstances, that antioxidants would exert their usual antioxidant action, this was not found to be the case.

The oxygen-absorption experiments were all made by the direct constant-pressure method. Observations were first made of the dark reaction over the temperature range 60° to 70° C, when the effect was obtained of an initial rapid absorption (not a solubility effect), followed by a constant rate of absorption of at least 60 hours duration. When the mass of oxygen absorbed per gram of rubber ($m$) is plotted against time, it is assumed that the intercept of the constant rate curve on the $m$-axis represents the mass of oxygen required to react with the superactive (relatively more active) centers initially present per gram of rubber. The activity of these relatively more active centers appears to be affected by the addition of antioxidants in the same way as the less active portions of the rubber molecule.

Under the influence of light, the oxygen absorption of all the vulcanizates was shown to vary in a similar manner, consistent with the building up, in time, of a concentration of "light-activated" centers.

Another interesting observation was that with short periods of exposure there was no persistence of the activation, as observed by Morgan and Naunton[1], but with longer exposure persistent effects were observed; in other words, as might be expected, it is the quantity of light absorbed and not merely its intensity which gives rise to the effect.

In the course of this work the effect of the action of a mixture of antioxidant and deactivator, as described by Le Bras[2], was confirmed in the case of phenyl-$\beta$-naphthylamine and mercaptobenzimidazole, respectively. A most interesting observation was that in spite of the fact that PBN and MBI under the action of light do not retard the uptake of oxygen, their combined use does result

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in a reduction of oxygen absorption; in other words, although antioxidants (of the PBN type) are ineffective against light activated absorption, the Le Bras effect of mixed antioxidants and deactivators still appears to hold good.

## EXPERIMENTAL

The stainless-steel oxidation cell was that used by Horrobin, New, and Taylor[3], with a modified manometer system. The cell face was closed by a plane glass plate and sealed with a very thin polythene gasket. Connection to the manometer system was made through a ground-glass hemispherical joint, which allowed easy detachment of the manometer from the cell, and which reduced the intervening dead-space to a minimum. The manometer system consisted of two calibrated tubes 80 cm. long, both connected to a common mercury reservoir. One tube was open to the atmosphere. Both tubes were enclosed in the same glass water-jacket and maintained at the same temperature as the reaction-cell by a water circulation controlled to $\pm 0.2°$ C. The oxygen manometer was drawn to a capillary at its upper end to facilitate observations of the vacuum-tightness of the apparatus.

In the light experiments white light from a 150 watt tungsten arc lamp giving a point source, was stopped down by a 4-cm. diameter aperture, filtered through 0.5 per cent copper sulfate solution and focussed as a 3-cm. diameter disc on the vertical front face of the oxidation cell. Relative light intensities were measured on a photoelectric cell. The optical system was of glass.

A blank oxidation cell was dispensed with since, to be effective, such a blank cell with its own manometer system must be identical with the active unit. Identity is difficult to achieve and, moreover, the volume of the blank cell has to be readjusted in every run to allow for the different volumes of the various rubber samples used. In the volumetric measurement of very small quantities of oxygen it is, therefore, likely that the use of a blank comparison cell reduces the experimental accuracy. Accordingly, in the present direct method, atmospheric pressure was continuously observed on a microbarograph calibrated directly against a standard mercury barometer. To confer stability a fairly wide manometer tube (6 mm. in diameter) was used, and the rise of the mercury was followed with a cathetometer. The oxygen pressure was maintained at the observed atmospheric pressure during absorption by frequent adjustments of the mercury reservoir. The sensitivity of the method was of the order $10^{-5}$ gram oxygen per millimeter of mercury, and rates of oxygen absorption of the order $10^{-5}$ gram oxygen per gram of rubber per hour could be observed with a total experimental error of less than 1 per cent.

The experimental procedure was as follows. Sheets of the vulcanizates less than 1 mm. thick were prepared and stored in darkness in an atmosphere of carbon dioxide. Sample discs 4 cm. in diameter were cut in dim light, weighed, and placed in the oxidation cell maintained at the desired temperature. The apparatus was then evacuated until a residual pressure of less than 0.1 mm. mercury was held constant in the manometer, indicating the gas tightness of the various joints and the effective removal of dissolved gases from the sample. The apparatus was then flushed out a few times with dry oxygen and finally filled with oxygen at atmospheric pressure. After solubility equilibrium had been attained, the absorption of oxygen (in grams $\times 10^{-4}$) was plotted against time in hours. The dark oxidation curve of all the vulcanizates was obtained at 60°, 65°, and 70° C.

The same initial procedure up to the attainment of temperature and solubil-

ity equilibrium was followed in the case of the light experiments. Subsequently two variations were made. In the first, the light was switched on immediately; in the second the light was switched on only when the dark reaction had attained its constant rate. The light experiments were made at the same three temperatures, 60°, 65°, and 70° C. From the measured transmission curves of the vulcanizates to the light used, a total thickness of 2 mm. was found to be necessary for complete absorption of the light. Hence in all the light experiments three samples were used giving a total thickness of more than 2 mm. In this way assumptions as to the amount of light transmission through the sample and reflection from the back face of the cell were avoided; at the same time a thickness of less than 1 mm. was maintained in the oxygen-absorbing samples.

At the end of every oxidation run the apparatus was "frozen" by quickly reducing the temperature through 40° to 50° C; the mass of oxygen was recalculated, the apparatus then evacuated, and the vacuum-tightness observed. In this way the experimental error was checked over a wide range of volume and temperature, and the cell face checked for leakage. This is an important point, since it had been shown in preliminary experiments that minute leakage at the cell face, though not suppressing the absorption effect, could produce a quite spurious oxidation curve.

The vulcanizates used had the following composition, and were vulcanized in hot molds for 24 minutes at 134° C:

| | | | | |
|---|---|---|---|---|
| Pale crepe | 100 | — | — | — |
| Stearic acid | 1 | — | — | — |
| Zinc oxide | 5 | — | — | — |
| China clay | 10 | — | — | — |
| Tetramethylthiuram disulfide (TMT) | 0.2 | — | — | — |
| Benzothiazoyl disulfide (MBTS) | 0.25 | — | — | — |
| Sulfur | 2.5 | — | — | — |
| Phenyl-β-naphthylamine (PBN) | — | 2 | — | 1 |
| Mercaptobenzimidazole (MBI) | — | — | 2 | 1 |

## DISCUSSION OF EXPERIMENTAL RESULTS

### THE DARK REACTION

With sheets less than 1 mm. thick and oxygen pressure maintained at one atmosphere during absorption, diffusion of oxygen into the rubber was not expected to be a rate-controlling process in the oxidation reaction. This was confirmed by comparison with the oxidation curve of finely divided vulcanizate, when quite negligible differences were observed.

In all the cases examined, an initial rapid intake of oxygen was followed by a lower rate, which was constant to at least 60 hours. Figure 1 is typical of these dark curves, and shows the mass of oxygen absorbed per gram of rubber against duration of oxidation. All the dark curves can be represented by the general equation:

$$m = m_0 (1 - e^{-K_1 t}) + K_2 t$$

where $K_1$ and $K_2$ are the rate constants for the initial rapid and slower constant reaction, respectively. This analysis has been made for the vulcanizates at the three temperatures of observation, the equations giving good agreement with the experimental curves. When $m$ and $m_0$ are expressed in gram oxygen $\times 10^{-4}$ per gram of rubber and $t$ in hours, the following tables show the calculated values of $K_1$ and $K_2$:

TABLE 1.—$K_1$

| Temp. (° C) | Control | PBN | MBI | Mixt. (PBN, MBI) |
|---|---|---|---|---|
| 70 | 0.194 | 0.101 | 0.227 | 0.100 |
| 65 | 0.135 | 0.165 | 0.114 | 0.115 |
| 60 | 0.118 | 0.195 | 0.151 | 0.188 |

TABLE 2.—$K_2$

| Temp. (° C) | Control | PBN | MBI | Mixt. (PBN, MBI) |
|---|---|---|---|---|
| 70 | 0.292 | 0.142 | 0.336 | 0.154 |
| 65 | 0.160 | 0.103 | 0.165 | 0.084 |
| 60 | 0.117 | 0.061 | 0.096 | 0.059 |

$K_2$ is, of course, the constant rate of absorption (grams oxygen $10^{-4}$/gram rubber/hour) which succeeds the initial more rapid absorption. Table 2 is summarized in Figure 2 which shows the variation in constant rate of oxidation with temperature. Figure 2 shows the separation of the antiaging substances into two classes:

(1) MBI, which has little effect on the rate of oxygen uptake of the control, and which may even promote oxygen absorption at higher temperatures.

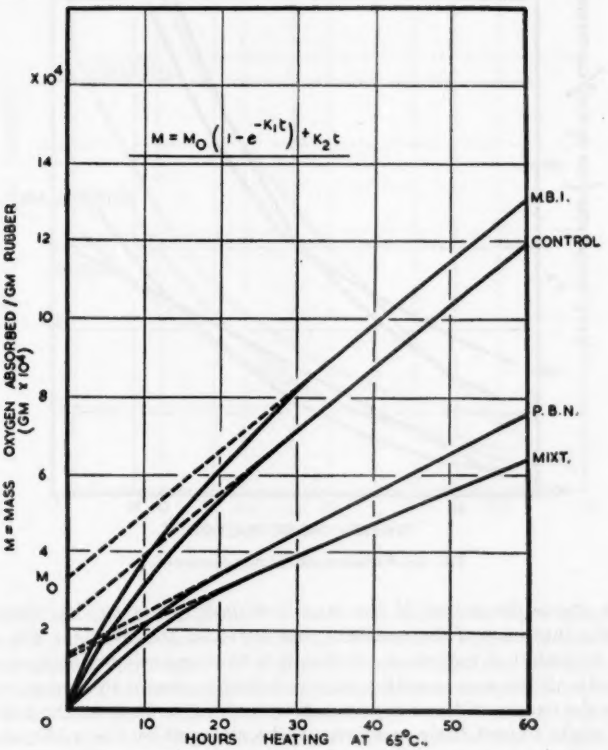


FIG. 1.—Absorption curves. Dark 65° C.

(2) PBN and the mixture (PBN, MBI), which suppress the oxygen absorption of the control. There is little difference in the effects produced by PBN alone and in combination with MBI, although there is a suggestion that PBN alone would be more effective at higher temperatures in suppressing oxygen absorption.

This broad division between MBI and PBN (alone and in combination with MBI) is in general agreement, as regards oxygen absorption, with Le Bras' theory of the mode of action of MBI and PBN, but the precise temperature variation of the effect appears to be more complicated.

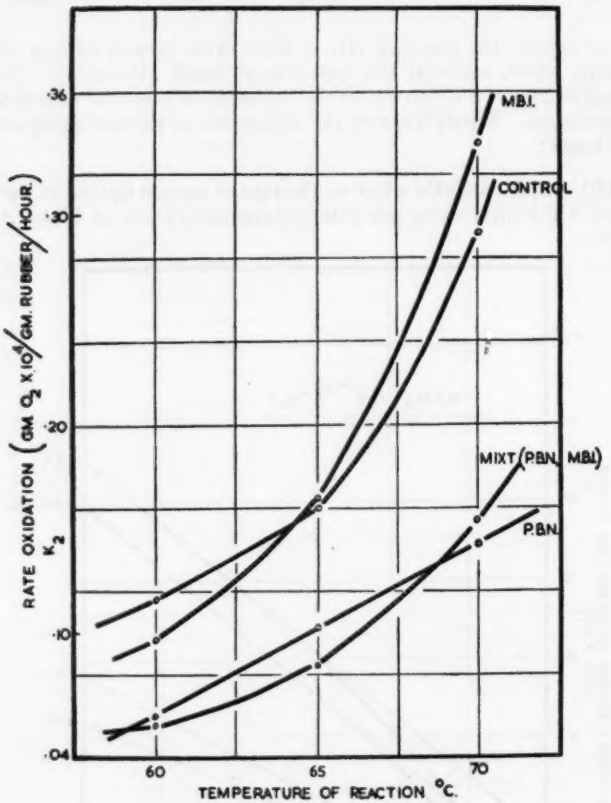


FIG. 2.—Variation rate with temperature.

In the above discussion of the standard dark curve, $m_0$ has simply been taken as the intercept of the constant rate curve on the $m$-axis. The simplest postulate to make[4] as regards $m_0$ is that it is that quantity of oxygen required to react with all the superreactive centers initially present in a gram of rubber. Whatever the nature of these superreactive centers, or their method of production, one might expect their reactivity to be changed by the addition of antioxidants, and also to vary with the life of the vulcanizate. The value of $m_0$ as

determined in all the dark oxidation runs were plotted against the dark storage life of the particular samples. Figure 3 shows the decay of what might be called the initial oxidizability of the vulcanizate. This Figure 3 shows also the relative effects on $m_0$ of the various antiaging substances. In this respect MBI appears to promote the reactivity of the superreactive centers, whereas PBN and the mixture (PBN, MBI) decrease the reactivity of these centers relative to the control. Qualitatively, then, the effect of antiaging substances on the

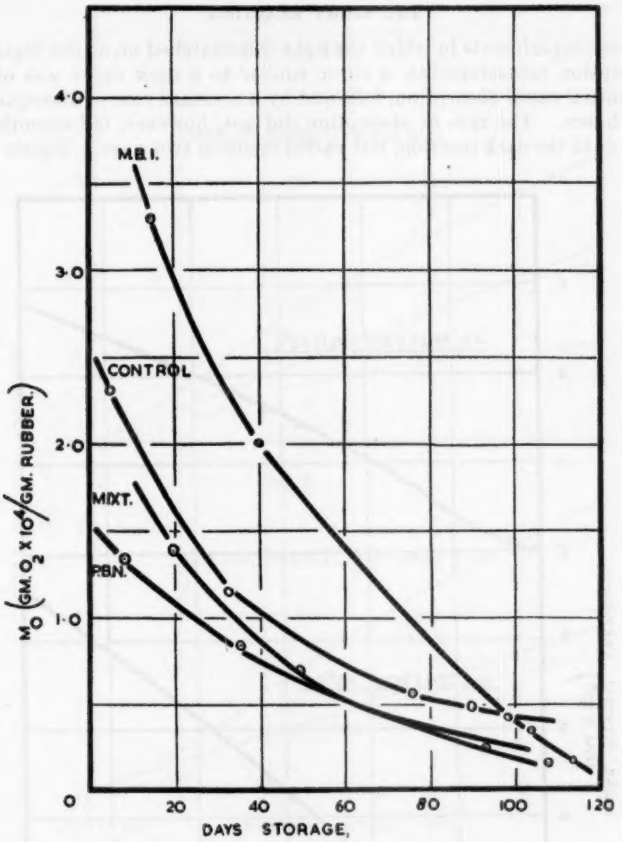


FIG. 3.—Decay of initial oxidizability.

thermal oxidation of the superreactive centers is similar to their effect on the less active portion of the rubber molecule. It further appears from Figure 3 that, as regards the suppression of the initial reaction, storage of the vulcanizates under carbon dioxide is useless; it is probable that oxygen incorporated in the mix during milling is sufficient to initiate and complete the decay of the superreactive centers, irrespective of the inert atmosphere used to suppress the major (second) reaction. Obviously, the particular value of $m_0$ found in any

oxidation run depends on the stored life of the sample used. The longer the periods of storage, the smaller is $m_0$, and the more difficult it becomes to calculate $K_1$ with any accuracy from the observed value of $m_0$. This accounts for the erratic variations of $K_1$ in Table 1.

Since the value of $m_0$ is a measure of the residual superoxidizability, comparisons of $m_0$ for the same mix, determined immediately after preparation, would give a comparison of the preoxidation suffered by the vulcanizate in, *e.g.*, milling processes.

### THE LIGHT REACTION

In those experiments in which the light was switched on at the beginning of the absorption measurements, a curve similar to a dark curve was obtained, *i. e.*, an initial rapid absorption, followed by a constant rate of absorption to at least 60 hours. The rate of absorption did not, however, fall smoothly from the start as in the dark reaction, but varied in one of two ways. Figure 4 shows

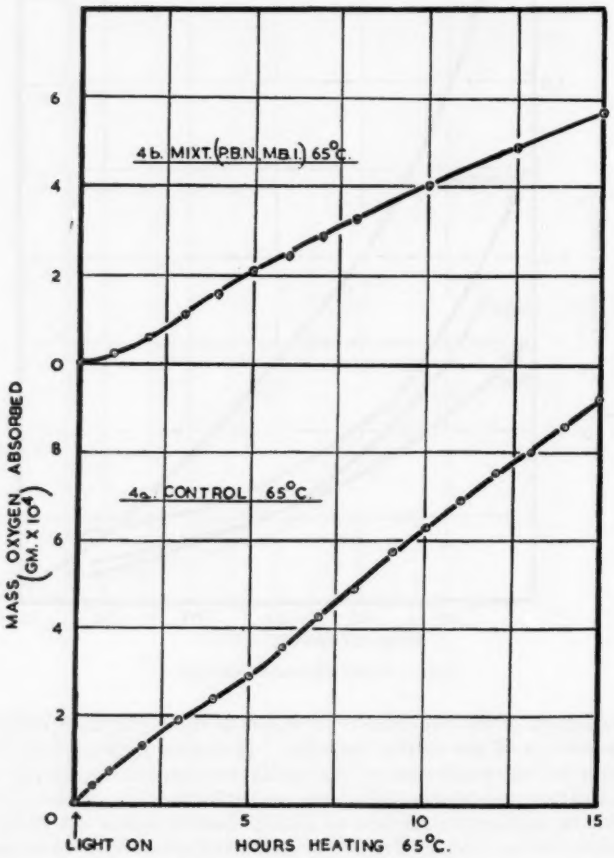


FIG. 4.—Initial absorption in light.

typical examples of these two types of initial absorption plotted as far as 15 hours. In one type (4a) the rate passes through a minimum and then a maximum before becoming constant, and in the second type (4b) the rate passes through a maximum only into a constant rate.

In subsequent experiments, the vulcanizates were first oxidized to the attainment of the constant dark rate before switching on the light. In these cases the effect of light was in all cases similar, and is illustrated by the typical curves

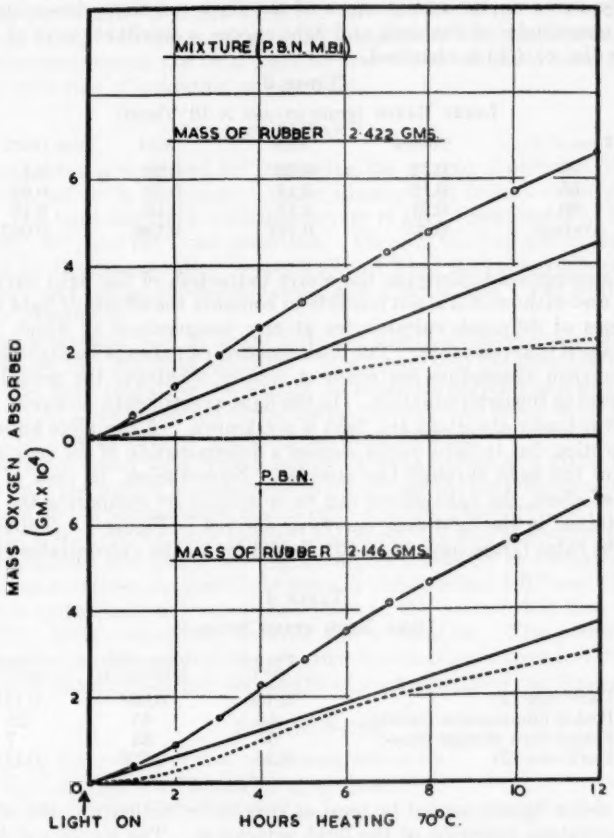


FIG. 5.—Derived light curves 70°C.

in Figure 5 plotted to 12 hours. From the moment of illumination, the previously established constant dark rate changes continuously through a maximum and becomes established after a few hours at a new constant value greater than the original dark rate. This mode of transition held for all the four vulcanizates in the range of temperature considered.

To extract the effect of the light along on the oxidation reaction, it has been assumed that the dark thermal reaction appropriate to the temperature is pro-

ceeding independently of the reaction promoted by the light. The oxygen-absorption curve of the sample due to the light alone is then represented in Figure 5 by the dotted curve, which is simply the subtraction of the established constant dark absorption from the total absorption under the influence of light. The effect of light alone, as used in these experiments, is then similar in all cases, *viz.*, a rate of oxygen absorption, initially zero, rising through a maximum and then falling to a constant rate.

The curves of Figure 4 now appear as the superposition of the standard light-only curve on the initial curve of the dark reaction; depending on the relative magnitudes of the dark and light curves, a resultant curve of the form of either 4(a) or 4(b) is obtained.

TABLE 3

LIGHT RATES (gram oxygen $\times 10^{-4}$/hour).

| Temp. (° C) | Control | PBN | MBI | Mixt. (PBN, MBI) |
|---|---|---|---|---|
| 70 | 0.22 | 0.22 | 0.23 | 0.11 |
| 65 | 0.19 | 0.18 | 0.18 | 0.08 |
| 60 | 0.21 | 0.19 | 0.16 | 0.10 |
| Average | 0.207 | 0.197 | 0.190 | 0.097 |

The assumption underlying the above extraction of the light curve is reasonable, and without it it is not possible to compare the effects of light on different masses of different vulcanizates at any temperature at which the dark reaction itself is appreciable. The dark reaction can always be expressed as the rate of oxygen absorption per gram of rubber, whatever the actual mass of rubber used in the determination. In the light experiments, however, the mass of rubber actually absorbing the light is not known. A complete knowledge of the absorption due to light would require a determination of the spectral transmission of the light through the samples. Nevertheless, in view of the uniformity of effect, the light effects can be compared by comparing the constant rates obtained in the light-only curves as derived in Figure 5. Table 3 shows these light rates (gram oxygen $\times 10^{-4}$/hour) for all the vulcanizates examined.

TABLE 4

DARK RATE AFTER STORAGE

| | Control 65° C | Mixt. (PBN, MBI) 65° C | Control 60° C |
|---|---|---|---|
| Dark rate (1) | 0.160 | 0.084 | 0.118 |
| Period illumination (hours) | 45 | 45 | 25 |
| Period dark storage (days) | 61 | 33 | 7 |
| Dark rate (2) | 0.23 | 0.082 | 0.117 |

The above figures cannot be used as conclusive evidence of the absence of any temperature variation of the light activation. The significant feature is that, although little difference is observed between the average values of PBN and MBI, the light-activated rate of absorption of the vulcanizate containing mixture (PBN, MBI) is about half the rate for PBN and MBI, separately. From this it appears that, as regards oxygen absorption, the mutual action of an antioxidant and a deactivating agent applies also to light-activated absorption.

In all the light experiments the rate of oxygen absorption recovered to its previous dark value within about 5 to 10 hours of switching off the light. In view of the observations of Morgan and Naunton[1] on the persistance of the

light effect, a few experiments were made to redetermine the dark rate after illumination followed by a period of dark storage in air at room temperature. Table 4 summarizes the results.

It appears from this that a minimum absorption of light energy is necessary to produce a persistent increase in the dark rate of oxidation. Once this is exceeded, large (44 per cent in case 1 above) persistent acceleration can be produced in unprotected mixes, and this would seriously affect bomb or oven-aging tests. Short periods of exposure to weak illumination would not affect such tests, particularly if the samples were given a few hours' rest in the darkness before aging. However, since large increases of rate can develop over a period of several weeks, the total light history of the sample is most probably reflected in its rate of oxidation at any time.

## SUMMARY

An apparatus is described for measuring the oxygen absorption of vulcanized rubber, either in darkness or under illumination from a controlled light source. The light and dark oxidation curves of four vulcanizates at temperatures of 60°, 65°, and 70° C are examined. Three of the four vulcanizates were protected by the incorporation, respectively, of 2 per cent phenyl-β-naphthylamine, 2 per cent mercaptobenzimidazole, and a mixture of 1 per cent each of the above substances.

The dark reaction over 60 hours' duration was in all cases similar and could be represented by a standard equation. It is shown that the effects of PBN and MBI on the dark oxidation are clearly different throughout the temperature ranges. From a consideration of the initial reaction, the decay during storage of the initial oxidizability of the vulcanizates is shown.

In oxidation under light from a relatively weak source at a given temperature, the total absorption is considered as the sum of the dark thermal oxidation appropriate to the temperature, and a light-activated absorption. The effect of the light is then shown to be similar in all cases, the rate of absorption due to light starting from zero and increasing through a maximum to a constant value. By comparison of these constant light rates, it is shown that PBN and MBI have little effect on the light-activated absorption of the control, but that the mixture (PBN, MBI) effectively reduces this absorption. The persistence or development of an enhanced dark rate after illumination is shown to depend on the period of illumination and the length of dark storage of the vulcanizate.

## REFERENCES

[1] Morgan and Naunton, *Proc. Rubber Tech. Conf.*, London, 1938, p. 613.
[2] Le Bras, *Rev. gén. caoutchouc 21*, No. 1, 3 (1944).
[3] Horrobin, New and Taylor, *Trans. Faraday Soc.* **42**, 252 (1946).
[4] Shelton and Winn, *Ind. Eng. Chem.* **38**, 75 (1946).

# INTERACTION BETWEEN POLYMERS AND FILLERS *

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In the literature the problem of whether or not filler particles adhere to a polymer is still under discussion. This point is already of interest in the mixing process because here the question resolves itself into whether the particles clog together or each becomes separately surrounded by polymer only[1]. The problem is also of paramount interest with regard to the properties of the final mixture because upon the interaction depends whether or not a filler has a reinforcing action. This is a key problem, especially in the rubber industry.

Essentially, the problem of dispersing a filler in a polymer is of the same type as that of dissolving a polymer in a solvent, and for the thermodynamic considerations we know that dispersing occurs if (leaving the entropy factor out of discussion) $\Delta U$($U$ = internal energy) is negative, that is, heat is liberated[2]. Here the historical measurements of Hock and his coworkers[3] show that, on mixing rubber with carbon black, 11 gcal. per gram of black (which is of the order of 1 gcal. per mole) extrapolated to zero concentration, are developed. This heat is found to decrease with increasing proportion of filler, showing that all particles are no longer in contact with the rubber because of clogging. It has long been a problem to explain the outstanding reinforcing properties of carbon black with the aid of these low values found by Hock.

Smith and Schaeffer[4] showed that the initial heat of adsorption between carbon black and $C_4$ hydrocarbons is of the order of magnitude of 15 kcal. per mole, decreasing sharply until about 40 per cent of a monolayer is formed. This indicates that 40 per cent of the carbon black surface is covered with sites of high adsorptive capacity. Between 40 and 100 per cent of this monolayer formation the surface appears to be quite uniform with regard to adsorptive capacity; at the monolayer the values again decrease and approach the heat of liquefaction, $E_L$, of the adsorbate. These results are shown in Figure 1. From the data obtained, it can be derived that the heat of adsorption per $CH_2$ group to carbon black is about 4 kcal./mole.

In our opinion these step-by-step adsorption experiments are keys to the explanation of the reinforcing action of fillers. They make it clear that the integral heat of adsorption measured by Hock never could lead to a proper understanding of the fundamental background. There may be forces of attraction and of repulsion on the carbon black particle, leading to negative and positive heats of adsorption. What Hock measures is the algebraic sum of these values, and so one may even find a positive heat (repulsive sites preponderating), although adhesion takes place on the spots of attraction. The measurements of Smith disclose the true situation and show that a limited number of sites of attraction may be responsible for the reinforcing effect. It is important to note that parts of these sites are of a relatively high energy content (15 kcal.), leading to strong bonds.

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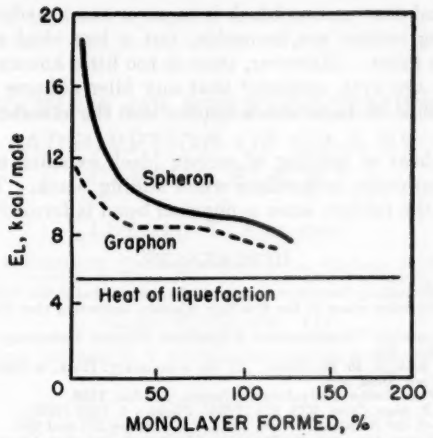


FIG. 1.—Heat of adsorption between carbon black MPC and 1-butene (0° C).

Such sites of high adsorptive capacity may be due to the attraction by certain atomic groups, but there exist also other factors leading to selective adsorption. De Boer and Custers[5] showed that, in the case of adsorption of gases by means of van der Waals' forces, the gain of energy is maximal when the molecule of the adsorbent can make a maximum number of contacts with the surface. Figure 2 shows the adsorption energies at various parts of a crystal, according to calculations by Kossel[6], from which it appears that the values in this simple case vary from 0.066 to 0.874, or by a factor of 13.

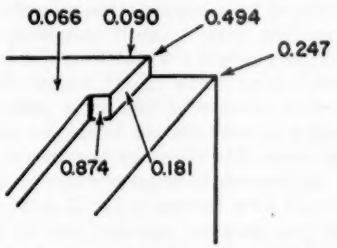


FIG. 2.—Van der Waals' adsorption energies at various sites of a NaCl crystal.

In contrast to this stands the adsorption by means of electrostatic forces, where the energy gain is maximal at sharp corners, sticking out of the surface.

If the surface of a normal crystal is observed microscopically, it appears that no flat surface is actually present[6]. Referring to the great number of crystallites[7] in a carbon black particle, an extremely uneven surface is to be expected here; one black particle may contain 1000 crystallites, with a length between 15 and 30 A. So one may assume a spectrum of adsorptive forces. This spectrum becomes still more complicated because of the different chemical composition of the surface at various spots. In this respect we refer to the presence of H, $CH_3$, COH, and COOH groups on one and the same carbon black particle.

Bearing in mind that carbon black is more or less a hydrocarbon, the conditions for wetting rubber are favorable, but a less ideal situation may be expected for other fillers. However, there is too little known to make definite statements; there are even opinions[8] that any filler adheres well to rubber if only the right method of dispersion is applied and the adsorbed air films can be removed.

The negative heat of wetting of carbon black explains why unvulcanized rubber becomes insoluble in gasoline when adding black. The latter cannot be loosened from the rubber, since a physical bond is formed[9].

## REFERENCES

[1] Drogin (*Proc. Rubber Technology Conference*, London **1948**) showed that in the mixing process the greatest change in viscosity takes place in the first four minutes, indicating that this time is necessary for proper mixing.
[2] For a summary, see Houwink, "Fundamentals of Synthetic Polymer Technology," Elsevier, New York-Amsterdam, **1949**, p. 50.
[3] Hartner, *Kolloidchem. Beihefte*, **30**, 83 (1930). *Cf.* for a summary: Hock, in Memmler, "The Science of Rubber," New York, **1934**, 505.
[4] Smith and Schaeffer, *Proc. Rubber Technology Conference*, London, **1948**.
[5] De Boer and Custers, *Z. phys. Chem.* **B25**, 225 (1934); *Physica*, **4**, 1017 (1937).
[6] See Schwab, "Handbuch der Katalyse," Wien, **1943**, Vol. 4, pages 271 and 281.
[7] Mrgudich and Clock, *Electrochem. Soc.* **29**, 29 (1944); Clark *et al. Ind. Eng. Chem.* **41**, 201 (1949).
[8] Endres, *Ind. Eng. Chem.* **16**, 1148 (1924).
[9] Le Blanc and Kröger, *Kolloidchem. Beihefte* **20**, 356 (1925).

# MECHANISM OF REËNFORCEMENT. IV. ADSORPTION OF GR-S BY CARBON BLACK *

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In earlier work[1] it has been shown that by treating a GR-S solution with reenforcing carbon black a specific fraction of the rubber is adsorbed, and a material whose physical properties differ markedly from those of the original sample is left in solution. The rubber not adsorbed has a higher modulus than the original untreated sample when compounded as pure-gum stock and a lower modulus when compounded with a reënforcing carbon black. This indicated that specific fractions of the rubber are adsorbed, and it was tentatively assumed that the fractions rich in styrene are preferentially adsorbed. This explanation is consistent with the behavior of the unadsorbed fractions of the samples, since, when compounded as pure-gum stock, a more uniformly vulcanizable matrix would be available, and this could show a higher modulus. The same samples, when compounded with carbon black, would have a lower modulus than comparable untreated samples, since less adsorbable material would be available to increase the effective volume of the reënforcing pigment.

It was of interest to attempt to verify this assumption by analysis of the fractions, and the obvious tool was infrared absorption. The results show that the specificity of adsorption is not in accord with the chemical composition of the copolymer. They do not indicate, however, any alternative explanation, which by elimination shows that the specificity of adsorption is in accord with the molecular weight. The low molecular-weight fractions are preferentially adsorbed.[2]

## PREPARATION AND TREATMENT OF SOLUTIONS

One-hundred milliliter portions of a solution prepared from 20 grams of commercial GR-S in 2000 milliliters of xylene were loaded with 1, 2, 4, and 8 grams of Cabot Grade 6 carbon black (surface area approximately 100 square meters per gram). For comparison with a coarse black, another one-hundred milliliter portion (1 gram GR-S in 100 ml. xylene) was loaded with 8 grams of Sterling R

* This paper was presented before the Division of Rubber Chemistry of the American Chemical Society, Atlantic City, September 21–23, 1949. It contains some of the experimental work of L. E. Amborski carried out in partial fulfillment of the degree of Master of Arts at the University of Buffalo.

furnace black (surface area approximately 25 square meters per gram). Another portion of the solution used as a control was carried through all the steps except for carbon black loading. The solutions were rotated and agitated in darkness for at least five days at room temperature.

The carbon black and adsorbed rubber were then separated from the solution by centrifuging for 6 to 8 hours in a Sorvall angle centrifuge at 12,000 revolutions per minute (average centrifugal force about 10,000 times gravity). The supernatant liquid was poured off and saved for infrared spectroscopic analysis. Only slight traces of carbon remained in the supernatant liquid; the clearest solutions being the ones with the highest loading of carbon black. Sutherland and Sheppard[3] have shown that the presence of carbon black in rubber, even at concentrations as high as 5 per cent, did not interfere with the infrared spectrum of rubber. It does produce a little scattering of the infrared radiation, however.

### FILM PREPARATION FOR SPECTROSCOPIC ANALYSIS

The treated GR-S solutions and the control were prepared for spectroscopic examination by concentrating them to a viscous mucilage, suitable for film spreading, by evaporating off the xylene in a vacuum oven at 70° C at a pressure of a few millimeters of mercury. Stirring (by hand) adequately eliminated gel formation due to localized evaporation. Films of relatively uniform thickness (approximately 0.02 mm.) were prepared on glass plates by spreading the concentrated mucilage with a film-casting knife, using a blade clearance of 1.5 mm. Fifteen to twenty minutes was allowed for evaporation of the solvent at room temperature. The films on the glass plates were then washed with methanol. This washing removed most of the residual xylene, which would interefere with the quantitative infrared analysis of the styrene fractions in the GR-S. The methanol also helped to lossen the film from the glass, thus facilitating its removal for mounting in the film holder, which consists of two rectangular pieces of aluminum $6\frac{3}{4} \times 1\frac{5}{8} \times \frac{1}{8}$ inches, between which the films are held. The two pieces are held together by screws and contain two holes, each $1\frac{1}{8}$ inch in diameter to permit passage of the infrared beam through the film sample. After being mounted in the film holder, which contained duplicate films, the samples were cleared of the last traces of solvent by heating in a vacuum oven at 70° C under a pressure of a few mm. of mercury for 8 to 16 hours. Films were then ready for spectroscopic analysis.

### INFRARED ANALYSIS

All spectroscopic measurements were made on a Beckman Model IR2 infrared spectrophotometer containing a rock salt prism. As recorded, the spectra (air blank and sample) consisted of a pair of traces measuring (as percentage full scale of the recorder chart) the energy transmitted by the film sample and by the air blank as a function of wave length (on a nonlinear scale). A percentage transmittance spectrum was obtained for each sample by measuring the ratios of the corresponding transmittance values (measured from percentage of full scale of charts for sample and air blank), and the spectrum was transcribed to linear wave-length charts, points being plotted every 0.05 microns. The absorption bands under consideration occurred between 8.5 and 15 microns, so the spectrum was studied over this range. Thus for each sample the percentage transmittance was plotted against wave length over the above-mentioned range.

*Method of quantitative spectral analysis*

The spectroscopic function employed to quantitatively measure the change in concentration of the chemical structure in question was the transmittance, $T$, of the sample as the experimentally measured quantity. To eliminate the dependance of $T$ on the thickness of the sample, which would have been impracticable to measure, the ratio of the extinctions at the wave lengths in

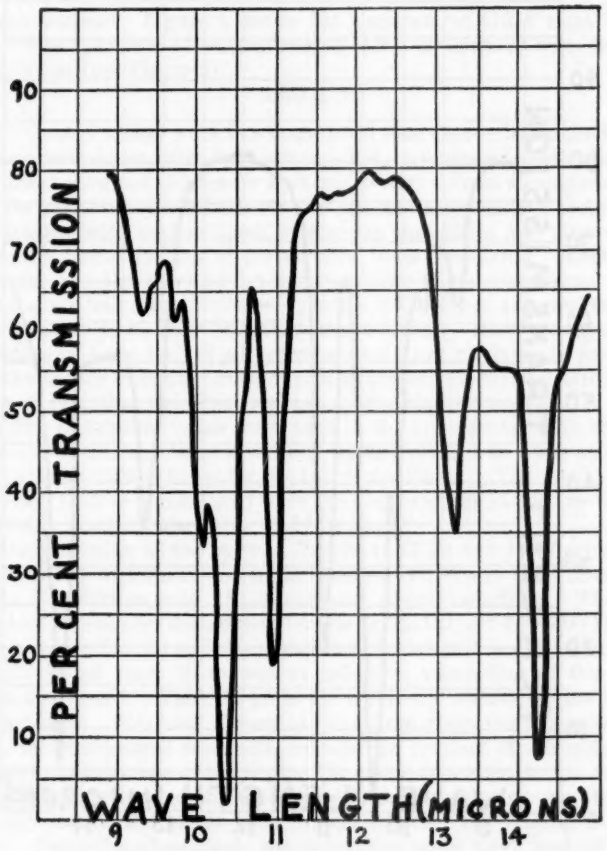


FIG. 1.—Infrared absorption spectrum of GR-S, percentage transmission *versus* wave length, 8.5 to 15 microns.

question was computed, since the thickness of sample is independent of wave length. For example, the ratio $\frac{E\ 13.20}{E\ 10.37}$ (subscripts refer to wave length) was determined for the untreated film. Any change in this ratio, then, for treated GR-S was a measure of the relative change of phenyl to 1,4-polybutadiene.

*Spectral-structural relationships of GR-S*

The chemical structures and the wave lengths of the maxima of the infrared absorption bands used in the analysis are given in Table I.

Thompson and Torkington[4] have shown that the strong 10.35 micron band is associated with the structure $R_1CH=CHR_2$ and that the 10.97 (and also weaker band at 10.05 microns) is associated with the structure $RCH=CH_2$ of a vinyl

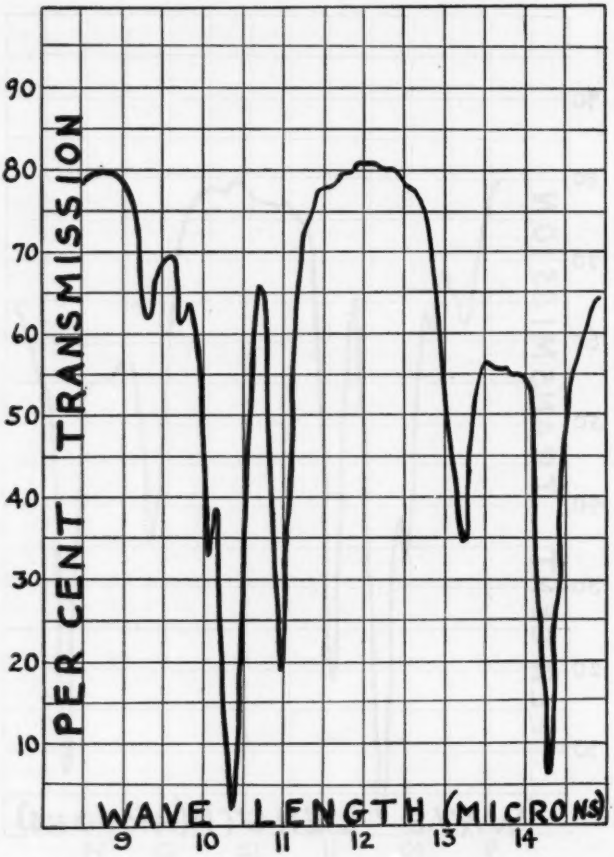


FIG. 2.—Infrared absorption spectrum of carbon-treated GR-S (8 grams Cabot Grade 6 carbon to 1 gram GR-S) percentage transmission *versus* wave length 8.5 to 15 microns.

group, all these bands arising from CH deformation vibrations. The relative intensities of these bands were used to determine the relative change in concentration of the 1,4- and 1,2-structures. Two bands were used to determine the concentration of polystyrene. These were the 14.3 micron band, which is characteristic of all monoalkylbenzenes, and the 13.2 micron band, which appears whenever the alkyl group differs from the methylene structure at the

TABLE I

IDENTIFICATION OF STRUCTURAL UNITS IN GR-S SPECTRUM

| Wave length (microns) | Structural unit |
|---|---|
| 10.08 | $-CH=CH_2$ (1,2-addition, vinyl) |
| 10.35 | $-HC=CH-$ (1,4-addition) |
| 10.97 | $-CH=CH_2$ (1,2-addition, vinyl) |
| 13.16 | $C_6H_5$ (phenyl) |
| 14.28 | $C_6H_5$ (phenyl) |

attachment carbon[4]. Figure 1 shows the spectrum of GR-S from 8.5 to 15 microns. The spectrum of carbon-treated GR-S is identical with that of the control polymer (see Figure 2).

## RESULTS

On the basis of earlier work it was assumed that carbon black preferentially adsorbed the polystyrene-rich fractions in GR-S, but infrared analysis of carbon-treated rubber gave no evidence for such selectivity. From a comparison of the ratios of the extinction coefficients for the various components of GR-S, treated and not treated with carbon black, it appears that there was no preferential adsorption by carbon for any of the chemical units considered. These include styrene units and the 1,2- and 1,4-addition units of polybutadiene. The experimental error was about 5 per cent; hence if there was any preferential adsorption, it must have been less than this amount. However, a change in concentration of 5 per cent of polystyrene would not produce the great differences in the tensile strength and modulus of the carbon-treated GR-S. Thus we must conclude that the selectivity is one of molecular weight.

Since two absorption bands were used in the analysis for both the phenyl groups (polystyrene) and the 1,2-addition units, a check was made on the work. Excellent agreement was found for the two comparisons. The small changes in concentration that were measured were not always in the same direction, so no trends for any possible selectivity could be found.

The concentration of the styrene (bands at 13.20 and 14.27 microns) was measured relative to 1,2-addition units (bands at 10.08 and 10.95 microns) and relative to 1,4-addition units (10.35 microns) of polybutadiene. The ratio of 1,2- to 1,4-units was also determined for the untreated and treated GR-S films. Both furnace (Sterling R) and channel (Grade 6, Cabot) blacks were used in the treatment. In all cases there was no selective adsorption of the chemical structures mentioned. Table II gives the individual results for the untreated and treated films. For each absorption band are given the percentage transmittance, the background transmittance and the product of the extinction coefficient and the thickness of the film. The ratios of the extinction coefficients given in the last section of the table were found by dividing the above mentioned products for the bands being compared, thus eliminating $T$, the film thickness. Several carbon-black concentrations were used, and in all cases there was no selectivity. The carbon-to-rubber ratios ranged from 1:1 to 8:1. In Table III the data are condensed, giving the averages for the duplicate films, together with the average deviation.

## SUMMARY

Infrared absorption analysis has been carried out to determine whether the adsorption of GR-S (co-polymer of polystyrene and polybutadiene) on carbon black is specific as to the chemical structure of the polymer. The comparison

## Table II

### GR-S Infrared Data

| Sample | Ratio Carbon rubber | 10.08 Microns (1, 2 Units) %T/Back. | Ext. | 10.37 Microns (1, 4 Units) %T/Back. | Ext. | 10.95 Microns (1, 2 Units) %T/Back. | Ext. | 13.20 Microns (Phenyl) %T/Back. | Ext. | 14.27 Microns (Phenyl) %T/Back. | Ext. | Ratio of extinction coefficients 10.37/10.08 | 10.37/10.95 | 10.37/13.20 | 10.37/14.27 | 10.95/13.20 | 10.95/14.27 | 10.08/13.20 | 10.08/14.27 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control No. 1 | — | 42.2/83.5 | .297 | 4.79/83.5 | 1.237 | 26.8/83.5 | .495 | 44.7/80 | .253 | 11.7 /68.5 | .768 | 4.17 | 2.50 | 4.89 | 1.61 | 1.95 | .645 | 1.17 | .388 |
| Control No. 2 | — | 48.2/81.5 | .229 | 8.44/81.5 | 0.986 | 33.8/81.5 | .384 | 50.1/77 | .188 | 17.75/67 | .578 | 4.31 | 2.57 | 5.25 | 1.71 | 2.04 | .665 | 1.22 | .396 |
| Control No. 3 | — | 37.6/81.5 | .336 | 3.97/81.5 | 1.314 | 22.4/81.5 | .562 | 40.7/77 | .277 | 10.6 /67 | .801 | 3.92 | 2.34 | 4.74 | 1.64 | 2.03 | .701 | 1.22 | .420 |
| Control No. 4 | — | 39.2/77.5 | .297 | 6.41/77.5 | 1.083 | 24.3/77.5 | .503 | 39.8/72.5 | .262 | 12.56/63.5 | .705 | 3.65 | 2.16 | 4.14 | 1.54 | 1.94 | .714 | 1.16 | .421 |
| Control No. 5 | — | 46.1/82.5 | .253 | 11.5 /82.5 | .858 | 36.1/82.5 | .360 | 48.3/77.5 | .207 | 21.4 /67.5 | .500 | 3.39 | 2.39 | 4.15 | 1.72 | 1.74 | .720 | 1.22 | .507 |
| Carbon Treated Grade 6 No. 1 | 1:1 | 43.5/82 | .275 | 6.23/82 | 1.121 | 28.4/82 | .462 | 46.7/77 | .218 | — | — | 4.08 | 2.45 | 5.19 | — | 2.12 | — | 1.26 | — |
| Carbon Treated Grade 6 No. 2 | 1:1 | 43.8/82 | .273 | 6.20/82 | 1.123 | 28.2/82 | .465 | 45.9/77 | .226 | — | — | 4.12 | 2.42 | 4.98 | — | 2.06 | — | 1.21 | — |
| Carbon Treated Grade 6 No. 1 | 2:1 | 33.4/79.5 | .378 | 2.60/79.5 | 1.487 | 19.4/79.5 | .613 | 35.3/73.5 | .319 | 6.61/65 | .993 | 3.93 | 2.42 | 4.66 | 1.50 | 1.92 | .617 | 1.18 | .381 |
| Carbon Treated Grade 6 No. 2 | 2:1 | 30.2/78.5 | .416 | 1.79/78.5 | 1.643 | 15.6/78.5 | .702 | 32.6/74 | .358 | 5.08/65 | 1.108 | 3.95 | 2.34 | 4.59 | 1.49 | 1.96 | .634 | 1.16 | .376 |
| Carbon Treated Grade 6 No. 1 | 4:1 | 32.9/81 | .392 | 2.34/81 | 1.540 | 18.2/81 | .650 | 34.4/75 | .340 | 5.87/66 | 1.052 | 3.93 | 2.37 | 4.53 | 1.46 | 1.91 | .617 | 1.15 | .373 |
| Carbon Treated Grade 6 No. 2 | 4:1 | 32.9/80 | .387 | 1.97/80 | 1.610 | 18.2/80 | .645 | 35.2/73.5 | .321 | 7.41/65 | .944 | 4.17 | 2.49 | 5.02 | 1.71 | 2.09 | .684 | 1.21 | .410 |
| Carbon Treated Grade 6 No. 1 | 8:1 | 24.8/75 | .482 | 1.07/75 | 1.847 | 11.3/75 | .824 | 25.4/74 | .464 | — | — | 3.84 | 2.24 | 3.98 | — | 1.78 | — | 1.04 | — |
| Carbon Treated Grade 6 No. 2 | 8:1 | 43.4/82 | .278 | 5.6 /82 | 1.167 | 29 /82 | .451 | 44.9/77 | .234 | — | — | 4.20 | 2.59 | 5.00 | — | 1.93 | — | 1.19 | — |
| Carbon Treated Sterling R No. 1 | 8:1 | 36.2/82.5 | .359 | 2.58/82.5 | 1.505 | 21.5/83 | .584 | 38.8/76 | .293 | — | — | 4.19 | 2.58 | 5.13 | — | 2.00 | — | 1.23 | — |
| Carbon Treated Sterling R No. 2 | 8:1 | 41.9/84 | .303 | 3.66/84 | 1.361 | 25.2/84 | .523 | 42.9/80 | .272 | — | — | 4.49 | 2.61 | 5.01 | — | 1.92 | — | 1.12 | — |

TABLE III

SUMMARY OF GR-S INFRARED DATA RATIOS OF EXTINCTION COEFFICIENTS

| Sample | GR-S control | GR-S Sterling R carbon | GR-S Grade 6 carbon | GR-S Grade 6 carbon | GR-S Grade 6 carbon | GR-S Grade 6 carbon |
|---|---|---|---|---|---|---|
| Ratio carbon GR-S | — | 8:1 | 8:1 | 4:1 | 2:1 | 1:1 |
| No. films tested | 5 | 2 | 2 | 2 | 2 | 2 |
| $\frac{1,4}{1,2}\ \frac{10.37}{10.08}$ | 3.89 ±.29 | 4.34±.15 | 4.02±.18 | 4.05 ±.12 | 3.94 ±.01 | 4.10±.02 |
| $\frac{1,4}{1,2}\ \frac{10.37}{10.95}$ | 2.39 ±.11 | 2.60±.02 | 2.42±.17 | 2.43 ±.06 | 2.38 ±0.48 | 2.44±.02 |
| $\frac{1,4\ \text{phenyl}}{10.37}$ | 4.63 ±.37 | 5.07±.06 | 4.49±.51 | 4.78 ±.24 | 4.63 ±.04 | 5.08±.10 |
| $\frac{1,4\ \text{phenyl}}{10.37}$ | 1.64 ±.06 | — | — | 1.58 ±.12 | 1.50 ±.00 | — |
| $\frac{1,2\ \text{phenyl}}{10.95}$ | 1.94 ±.08 | 1.96±.04 | 1.85±.08 | 1.96 ±.05 | 1.94 ±.02 | 2.09±.03 |
| $\frac{1,2\ \text{phenyl}}{10.95}$ | .689±.027 | — | — | .650±.34 | .623±.08 | — |
| $\frac{1,2\ \text{phenyl}}{10.08}$ | 1.20 ±.02 | 1.16±.04 | 1.12±.07 | 1.18 ±.03 | 1.17 ±.01 | 1.24±.03 |
| $\frac{1,2\ \text{phenyl}}{10.08}$ | .426±.032 | — | — | .391±.180 | .378±.02 | — |

of the relative intensities of the characteristic absorption bands of the original GR-S with the ratios of the intensities of the same bands for the fraction of rubber remaining after certain fractions were specifically removed by carbon black has shown that the adsorption is not specific as to chemical structure within the limits of accuracy of infrared analysis. The particular chemical groups considered were the phenyl structure (infrared absorption at 13.20 and

14.27 microns) of polystyrene and the 1,2 (10.08 and 10.95 microns) and 1,4 (10.37 microns) addition units of butadiene.

## ACKNOWLEDGMENT

We are indebted to the Rayon Technical Division of E. I. du Pont de Nemours and Company, whose facilities and equipment were made available and used in this work. Financial assistance was received through the Frederick Gardner Cottrell Special Grant-in-Aid of Postwar Scientific Research.

## REFERENCES

[1] Goldfinger, RUBBER CHEM. & TECHNOL. **18**, 286 (1945); *J. Polymer Research* **1**, 58 (1946).
[2] Mark and Saito, *Monatsh.* **68**, 237 (1936).
[3] Sutherland and Sheppard, RUBBER CHEM. & TECHNOL. **19**, 66 (1946).
[4] Thompson and Torkington, *Trans. Faraday Soc.* **41**, 246 (1945).

# OXYGEN ABSORPTION OF VULCANIZATES

## A MEANS OF EVALUATING AGING RESISTANCE *

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It is recognized[1] that the principal cause of deterioration of rubber is an oxidative one. The present study confirms previous information to the effect that rates of oxygen uptake by a rubber stock may be correlated, at least roughly, with the extent of deterioration caused by accelerated aging and by natural aging. Because of natural deleterious effects other than by oxygen, such as by stretching, ozone, ultraviolet light, heat, and pressure, no rapid aging method can be expected to do more than approximate the reaction of a rubber stock to its service environment.

Despite the nonquantitative nature of rapid evaluations of service life, such tests are of value to compounders, purchasers, and research workers because of the basis which they provide for comparison of similar stocks. In view of the lack of correlation between standard aging procedures[2], the question may well arise as to which method to use. In the absence of a compelling reason to choose one procedure over another, bomb aging has been used most commonly because of its advantage of rapidity.

The purpose of this paper is to show that routine volumetric measurement of rates of oxygen absorption of vulcanizates can give comparisons which, for control purposes, are at least as adequate as those provided by standard procedures and are a considerable saving of time and apparatus.

## PROCEDURE

Eight vulcanizates, including two natural and six synthetic stocks, were prepared according to the formulations in Table I. Tensile test-specimens were die-cut from sheets approximately 6 × 6 × 0.08 inches. Specimens were aged in a circulating air oven at 70° C for periods of 3, 7, 14, 21, and 28 days and in a Bierer-Davis pressure bomb at 70° C under 300-pound per square inch oxygen pressure for periods of 1, 3, 7, and 14 days.

Sufficient specimens for all aging periods were suspended in the aging chamber, one stock at a time. At the expiration of each time interval, six specimens were removed and the physical properties measured. As only a small number of samples were used, precautions were taken to minimize loss of statistical validity by use of a Latin square-type randomization technique. No two specimens from a group of sextuplicates were cut from the same sheet or from the same relative position on different sheets. Further precautions were taken in positioning specimens during aging, in order to eliminate, through randomization, possible effects of small temperature and air rate gradients.

The sheet material remaining after the test-specimens had been cut out was utilized for oxygen absorption measurements. It was composited and ground

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TABLE I

STOCK FORMULATIONS

| Stock 1<br>Hevea without antioxidant, cured 30 min. at 290° F | |
|---|---|
| Smoked sheet | 100.0 |
| Zinc oxide | 5.0 |
| Pelletex | 2.0 |
| Stearic acid | 1.0 |
| Cottonseed oil | 2.5 |
| Heliozone | 3.0 |
| D.O.T.G. (di-*o*-tolylguanidine) | 1.0 |
| Sulfur | 3.0 |

| Stock 2<br>Hevea with antioxidant, cured 30 min. at 290° F | |
|---|---|
| Smoke sheet | 100.0 |
| Zinc oxide | 5.0 |
| Pelletex | 2.0 |
| Stearic acid | 1.0 |
| Cottonseed oil | 2.5 |
| Heliozone | 3.0 |
| D.O.T.G. (di-*o*-tolylguanidine) | 1.0 |
| Sulfur | 3.0 |
| AgeRite Resin D | 1.0 |

| Stock 3<br>Polychloroprene without antioxidant, cured 30 min. at 310° F in hydraulic press plus 40 min. at 310° F in steam autoclave | |
|---|---|
| GR-M | 100.0 |
| Zinc oxide | 1.0 |
| XLC magnesia | 4.0 |
| P-33 | 30.0 |
| Stearic acid | 1.0 |
| Paraffin | 2.0 |
| Circo light process oil | 15.0 |
| Neophax-A | 5.0 |

| Stock 4<br>Polychloroprene with antioxidant, cured 30 min. at 310° F in hydraulic press plus 40 min. at 310° F in steam autoclave | |
|---|---|
| GR-M | 100.0 |
| Zinc oxide | 1.0 |
| XLC magnesia | 4.0 |
| P-33 | 30.0 |
| Stearic acid | 1.0 |
| Paraffin | 2.0 |
| Circo light process oil | 15.0 |
| Neophax-A | 5.0 |
| Neozone-A | 2.0 |

| Stock 5<br>GR-S, cured 20 min. at 310° F | |
|---|---|
| GR-S | 100.0 |
| Statex-B | 50.0 |
| Zinc oxide | 5.0 |
| Naftolen-510 | 20.0 |
| Heliozone | 3.0 |
| Thionex | 2.0 |
| D.P.G. (diphenylguanidine) | 0.4 |
| Sulfur | 0.6 |

| Stock 6<br>Butadiene-acrylonitrile copolymer, cured 25 min. at 310° F | |
|---|---|
| Perbunan-26 | 100.0 |
| Statex-B | 30.0 |
| P-33 | 30.0 |
| Zinc oxide | 5.0 |
| Stearic acid | 1.0 |
| Heliozone | 3.0 |
| Tributoxyethyl phosphate | 10.0 |
| Plasticizer-SC | 10.0 |
| Captax | 2.0 |
| Tuads | 3.0 |
| Vandex | 0.1 |

| Stock 7<br>Butyl, cured 30 min. at 310° F | |
|---|---|
| GR-I | 100.0 |
| Zinc oxide | 5.0 |
| Statex B | 50.0 |
| Stearic acid | 1.0 |
| Bayol-D | 10.0 |
| Captax | 0.5 |
| Tuads | 1.0 |
| Polyac | 1.0 |
| Sulfur | 2.0 |

| Stock 8<br>Polysulfide copolymer, cured 40 min. at 300° F | |
|---|---|
| Thiokol type FA | 100.0 |
| Zinc oxide | 10.0 |
| Pelletex | 40.0 |
| Stearic acid | 0.5 |
| D.P.G. (diphenylguanidine) | 0.1 |
| Altax | 0.3 |

in a Wiley mill. The resultant particle size was such that no dimension was greater than 0.5 mm., which was small enough to eliminate diffusion rate effects[3]. Considerable sample was introduced into the mill to accumulate the required amount of ground sample as rapidly as possible. In this way, the milling time was kept down to very short periods—of the order of 1 to 3 minutes. Absorp-

tion was allowed to proceed in oxygen at 1 atmosphere at a temperature of 120° C.

## ABSORPTION APPARATUS

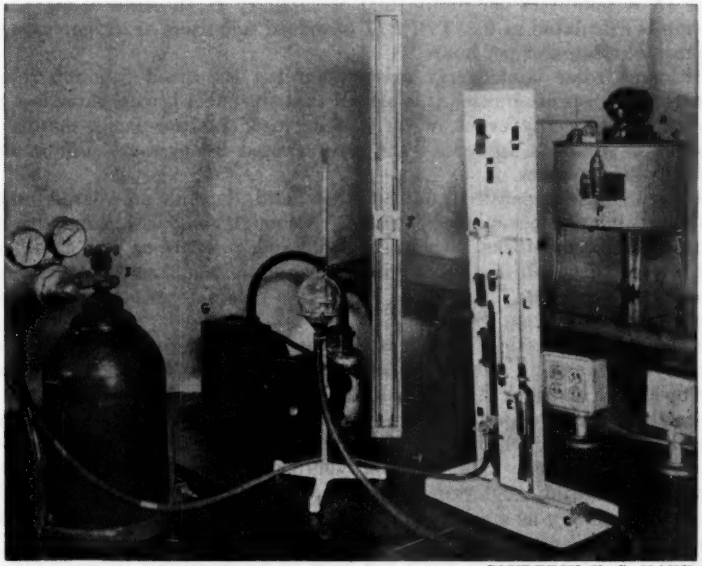
Oxygen absorption measurements were made in the apparatus pictured in Figure 1. This design is a modification of that used by van Amerongen[4].

The complete apparatus, as shown in Figure 1, consists of a measuring apparatus plus accessory equipment. These accessories are: an oxygen cylinder, *I;* a Cenco-Hyvac pump, *G;* a differential manometer, *J;* and a constant temperature oil bath, *H*. The bath was made by removing the viscometer tube from a Tag-Saybolt thermostatic viscometer and plugging the resulting hole in the bottom of the oil bath. The hole at the top was used to permit insertion of the absorption chamber, *F*, into the oil.

The measuring apparatus consists of three branches. The mercury reservoir, *E*, is connected: through a straight stopcock, *C*, to the mercury leveling bulb, *D;* through a calibrated capillary tube, *L*, to the absorption changer, *F;* and through another capillary tube, *K*, to either the atmosphere or the outer system, which consists of the manometer, *J*, and either oxygen, *I*, or vacuum, *G*.

The method of using the apparatus is as follows:

Start with one 3-way stopcock, *A*, open to the atmosphere, the other 3-way stopcock, *B*, in the closed position, and the straight stopcock, *C*, open. Adjust leveling bulb *D* until the mercury level is on a previously marked line on the mercury reservoir, *E*. Close *C*. Place a finely ground sample, of such size as to represent 1 gram of elastomer and contained in a small tube, in the oxidation chamber, *F*. Open *A* to the outer system. Open *B* to the operating vacuum



*COURTESY U. S. NAVY*

FIG. 1.—Oxygen absorption apparatus.

pump, *G*. When a full vacuum has been drawn, as indicated by the manometer, *J*, lift the entire measuring apparatus and place *F* in the 120° C constant temperature bath, *H*. Wait 10 minutes to allow the sample to come to thermal equilibrium.

Reverse the position of *B*, admitting oxygen from cylinder *I* at about 2- or 3-pound per square inch gage pressure. Start timing immediately on admitting the oxygen. Rapidly reverse *B*, and alternately evacuate and fill the system with oxygen twice more. When filling with oxygen for the last time, admit only enough to leave a vacuum of approximately 15 cm. of mercury, as indicated by *J*. Close *B*, open *C*, raise *D* until mercury rises into both capillaries, *K* and *L*, and open *A* to the atmosphere. Adjust the height of *D* so that the mercury levels in *K* and *L* are equal. Read the height on the scale and the elapsed time on an interval timer. The entire operation, from the first admission of oxygen to the first mercury level reading, should take less than 1 minute.

Continue to equalize roughly the levels in *K* and *L*, by adjusting the height of *D* throughout the determination. Never allow the levels to differ by more than 1 cm. At intervals of 10 minutes (or less, if the rate is rapid) accurately equalize the levels in *K* and *L* and read the height on the scale.

After 80 minutes (or less, if the rate is rapid) lower *D* until the mercury levels in *K* and *L* are near the bottom of the capillary tubes. Close *A*. Continue lowering *D* until both capillaries are empty of mercury. Open *A* to the atmosphere and close *C*. It is then safe to remove *F* from *H* and the oxidized sample from *F*. On opening *C*, the apparatus is immediately ready to be used for another determination.

The data, scale reading in millimeters against time in minutes, are plotted, and the slope of the straight line portion is measured in millimeters per hour, *R*. From the atmospheric temperature, *T*, and pressure, *P*, and the calibration factor (*F* = milliliters per millimeter) of capillary *L*, the rate of oxygen absorption is calculated as 0.359 $RFP/T$ standard milliliters of oxygen absorbed per gram of elastomer per hour.

Although some controversy exists regarding the exact function relating pressure and absorption rate[5], it is agreed that the effect is something less than proportional. In any event, when working near 1 atmosphere, manual adjustment is sufficient to reduce the error caused by pressure differences to negligibly small values.

A manometric apparatus[6], on the other hand, depends on a large pressure drop to attain even reasonable accuracy. Although comparisons may be made for nearly identical stocks, constantly decreasing pressure as well as different total pressure drops during individual determinations makes the utilization of manometric apparatus for absolute absorption rate determinations subject to criticism.

Aside from theoretical considerations, volumetric measurements are considerably more rapid. The apparatus described here may be used manometrically by closing stopcock *C* after the initial adjustment. Although this was not done in the reported experiments, the mercury in capillary *K* was lowered to its initial level at the conclusion of each determination and the final manometric reading was recorded. The ratio of volumetric to manometric change in mercury level during a determination ranged from 5.8 to 6.5. In short, utilization of the capillary as a microburet, rather than as a manometer, allowed attainment of a given capillary rise in one-sixth of the time.

Most oxygen absorption work has been at temperatures between 60° and 110° C. Carpenter[7] worked at lower temperatures, Dufraisse and Le Bras[8] at

120° C, and Mesrobian and Tobolsky[9] at 130° C. Other examples of high temperature absorption are incidental to work at more moderate conditions. To obtain greater rapidity a temperature of 120° C was used in all absorption measurements reported here. The use of a still higher temperature to reduce further the time required for a determination was not considered feasible because of the comparatively long period required for equilibration in those stocks containing volatile compounding ingredients.

The effect of temperature on absorption rate was considered only with the view of accelerating the test. Although it is reported[10] that above 100° C there may be a change in the oxidation mechanism of rubber, it is considered unlikely that such a change would be substantially different in similar stocks. Any changes in oxidation mechanisms of synthetic elastomers would probably occur at yet higher temperatures. For purposes of stock comparison, therefore, it was considered necessary to limit the test temperature only to a value which did not prove inconvenient from the standpoint of experimental technique.

## OXYGEN ABSORPTION RESULTS

Absorbed oxygen for the various stocks is plotted against time in Figure 2. The curves show individual characteristics. Stocks 1 and 2 show no deviation from linearity. There is no evidence of the autocatalytic nature of rubber oxidation. It may be that the lower portion of the *S* curve had been passed before initial readings were made, but the small amounts of oxygen absorbed in

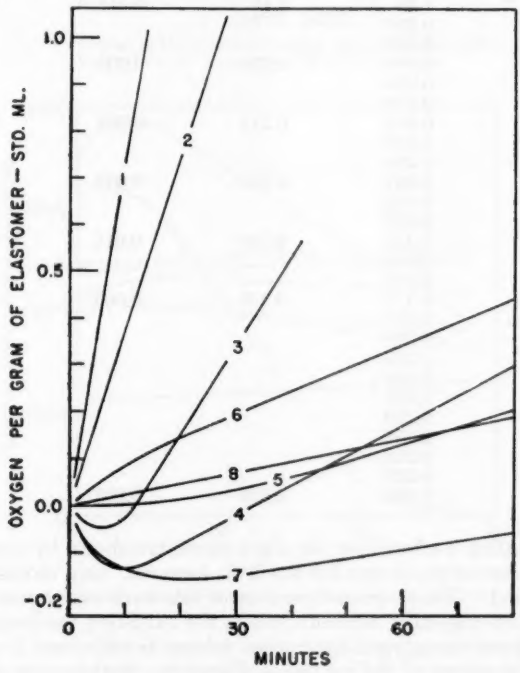



FIG. 2.—Rate of oxygen absorption, 120° C.

these experiments make it more likely that, even at the final reading, the linear portion of the curve had not been reached. If the latter view is correct, the apparent linearity is due to the fact that such a minute portion of the total absorption curve is reported. Stock 8 also shows a linear rate curve.

Stocks 3, 4, and 7 show an initial depression of the mercury column. This is due to evaporation of volatile compounding ingredients. As soon as the partial pressure equals the vapor pressure of the offending ingredient at 120° C, the curve assumes linearity. The reduction in oxygen partial pressure is not serious, *viz.*, of the order of 1 per cent in the worst case encountered.

TABLE II

OXYGEN ABSORPTION RATES

| Stock | Oxygen absorbed, std. ml. oxygen per hr. per g. elastomer | Mean | Mean deviation | % Deviation |
|---|---|---|---|---|
| 1 | 4.55 | | | |
| | 4.63 | | | |
| | 4.53 | 4.57 | 0.040 | 0.9 |
| 2 | 2.34 | | | |
| | 2.35 | | | |
| | 2.31 | 2.33 | 0.016 | 0.7 |
| 3 | 1.16 | | | |
| | 1.20 | | | |
| | 1.20 | 1.19 | 0.017 | 1.4 |
| 4 | 0.394 | | | |
| | 0.383 | | | |
| | 0.394 | 0.390 | 0.005 | 1.3 |
| 5 | 0.230 | | | |
| | 0.210 | | | |
| | 0.215 | 0.218 | 0.008 | 3.7 |
| 6 | 0.323 | | | |
| | 0.305 | | | |
| | 0.302 | 0.310 | 0.009 | 2.9 |
| 7 | 0.132 | | | |
| | 0.107 | | | |
| | 0.132 | 0.124 | 0.011 | 8.9 |
| 8 | 0.145 | | | |
| | 0.142 | | | |
| | 0.151 | 0.146 | 0.003 | 2.1 |
| 5X | 0.217 | | | |
| | 0.229 | | | |
| | 0.213 | | | |
| | 0.219 | | | |
| | 0.233 | | | |
| | 0.200 | | | |
| | 0.242 | | | |
| | 0.223 | | | |
| | 0.223 | | | |
| | 0.226 | 0.223 | 0.008 | 3.7 |

No explanation is offered for the slight curvature shown by stock 6 near the origin. The curvature shown by stock 5, however, may indicate a genuine induction period. The scope and purpose of this work were not such as to give any information regarding autocatalysis in the oxidation mechanism of GR-S.

Table II gives the oxygen absorption values, as calculated from the slopes of the linear portions of the curves in Figure 2. Satisfactory precision was obtained for all stocks except stock 7. This exception appears to be caused by

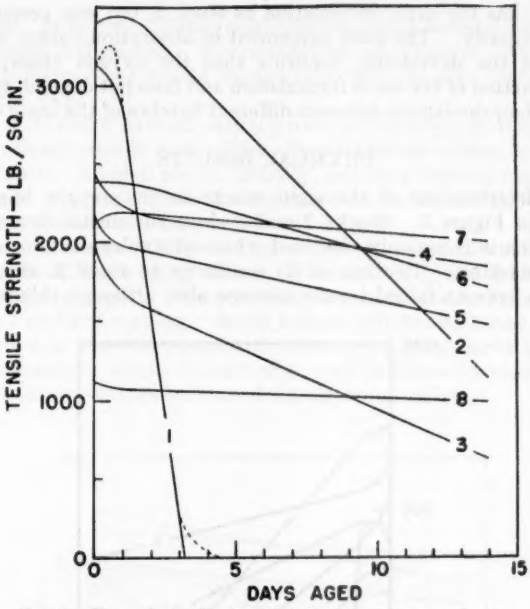



FIG. 3.—Change in tensile strength during aging in oxygen bomb. Temperature, 70° C; pressure, 300 lb. per sq. inch.

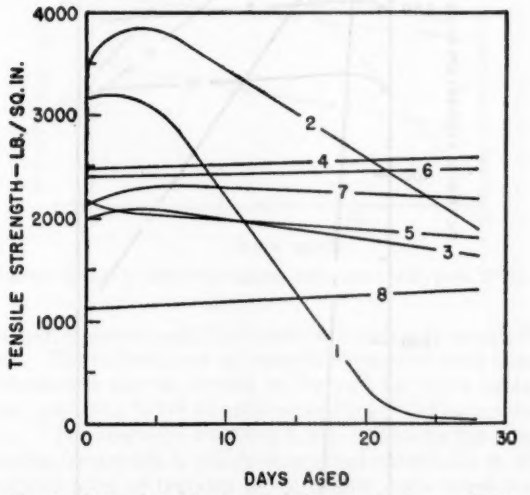



FIG. 4.—Change in tensile strength during aging in air oven, 70° C.

one bad run. To establish the best value for the oxygen absorption rate of stock 7, a replacement run would be indicated. This, however, would sacrifice the routineness of the determinations and was not done. Only three runs were made for each stock, and all values are reported.

Stock 5X has the same formulation as stock 5, but was prepared and run one year previously. The good agreement of absorption values, and excellent agreement of the deviations, confirms that the oxygen absorption rate is actually a function of the stock formulation and does not depend, to any serious extent, on minor deviations between different batches of the same stock.

## PHYSICAL RESULTS

Tensile deterioration of the eight stocks in the oxygen bomb is shown graphically in Figure 3. Stocks 2 and 7 show the initial increase in tensile strength which is commonly observed when aftervulcanization occurs during the aging procedure. Because of its similarity to stock 2, stock 1 may be presumed to have an initial tensile increase also, although this is not evident

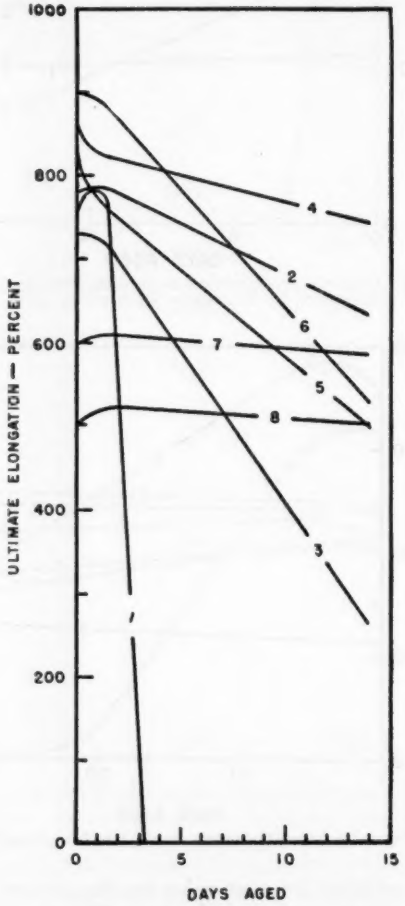



FIG. 5.—Change in ultimate elongation during aging in oxygen bomb. Temperature, 70° C; pressure, 300 lb. per sq. inch.

from the data. In addition, theoretical considerations demand a slowing down of rate at the end of the curve. The dotted portions of curve 1 probably represent a truer picture of the tensile change than does the solid curve which was drawn from the data.

Stocks 3, 4, 5, and 8 have an initial period of rapid loss in tensile strength, followed by a slower, steady rate. This effect is far less evident in stock 8 than in the other three. Stock 6 shows, initially, neither a rise nor rapid decline of tensile strength. Instead, there is a short period during which the deterioration rate is less than its ultimate value.

Oven aging, as shown in Figure 4, gives curves whose characteristics differ somewhat from the bomb aging curves. Stocks 1, 2, 3, and 7 have an initial increase in tensile strength. This represents a reversal in the behavior of stock 3, as compared with bomb aging. Stock 1 shows a flattening of the curve, which compares favorably with the postulated dotted portions of curve 1 in Figure 3. The initial increase for stocks 2 and 7 and rapid decrease for stock 5 show retention of the characteristics evidenced during bomb aging.

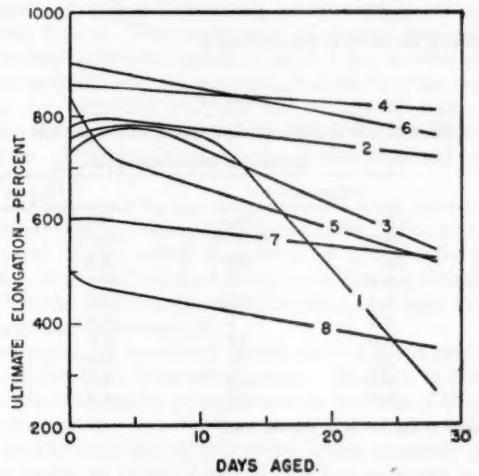



FIG. 6.—Change in ultimate elongation during aging in air oven, 70° C.

Stocks 4, 6, and 8 give a small, but positive, increase in tensile strength during oven aging. The curves show no sensible departure from linearity.

Ultimate elongation curves, plotted in Figure 5 for bomb aging and Figure 6 for oven aging, generally follow the characteristics of the corresponding tensile strength curve. The exceptions are stock 3, which reverses the initial curvature during bomb aging, and stock 8, which shows that effect both in the bomb and oven. No positive rates of increase in elongation were noted for any of the stocks during either bomb or oven aging.

Tables III and IV summarize the data for changes in tensile strength and ultimate elongation, respectively. The first and third columns of both tables list the rates of decrease of the appropriate physical property, as calculated from the slopes of the linear portions of the various curves.

In the usual determination of resistance to accelerated aging, no effort is made to establish steady rates of deterioration, *i.e.*, after the initial effects have disappeared. Instead, the total change during a fixed period is determined. This net change, of course, may include an initial increase, followed by a subsequent decrease.

TABLE III

EFFECT OF AGING ON TENSILE STRENGTH

| | Decrease in tensile strength, % | | | |
|---|---|---|---|---|
| | Oxygen bomb | | Air oven | |
| Stock | Per day[a] | After 96 hours | Per day[a] | After 28 days |
| 1 | 40 | 93[b] | 6.0 | 97 |
| 2 | 5.1 | 15 | 2.5 | 45 |
| 3 | 3.9 | 29 | 1.0 | 19 |
| 4 | 1.1 | 16 | −0.1 | − 5 |
| 5 | 1.8 | 17 | 0.5 | 20 |
| 6 | 2.3 | 7 | −0.1 | − 3 |
| 7 | 0.7 | 0 | 0.2 | − 5 |
| 8 | 0.6 | 5 | −0.3 | −13 |

[a] From linear portions of the curves in Figures 3 and 4.
[b] After 72 hours.

TABLE IV

EFFECT OF AGING ON ULTIMATE ELONGATION

| | Decrease in ultimate elongation, % | | | |
|---|---|---|---|---|
| | Oxygen bomb | | Air oven | |
| Stock | Per day[a] | After 96 hours | Per day[a] | After 28 days |
| 1 | 53 | 82[b] | 3.8 | 66 |
| 2 | 1.6 | 5 | 0.4 | 10 |
| 3 | 5.1 | 10 | 1.5 | 26 |
| 4 | 0.7 | 7 | 0.3 | 7 |
| 5 | 3.0 | 17 | 1.6 | 36 |
| 6 | 3.1 | 11 | 0.6 | 16 |
| 7 | 0.9 | −2 | 0.5 | 13 |
| 8 | 0.7 | −2 | 0.9 | 30 |

[a] From linear portions of the curves in Figures 5 and 6.
[b] After 72 hours.

To evaluate the stocks according to some standard procedure, the net decreases in tensile strength and ultimate elongation are presented in the second and fourth columns of Tables III and IV, respectively. The aging periods used are 96 hours in the oxygen bomb and 28 days in the air oven.

## CHEMICAL CHANGES DURING AGING

Acetone extractables are reported to increase when natural rubber ages. The alcoholic potassium hydroxide extract, according to Van Rossem and Dekker[11], is very sensitive to oxidation of the rubber, and increases long before the acetone extract. It seemed desirable to investigate the change in amount of extractables as aging progressed in the eight stocks.

After tensile strength and elongation measurements were made, each group of sextuplicate tensile specimens was cut up, and triplicate 1-gram composite samples were removed for extraction. The samples were first extracted for a

period of 8 hours with a mixture of 32 parts of acetone and 68 parts of chloroform by volume[12]. After drying, the alcoholic potassium hydroxide extracts were determined[13]. Both the acetone-chloroform and alcoholic potassium hydroxide extracts were determined for each aging period in the bomb and oven.

The expected progressive increases in extractables were not found. Although those stocks containing volatile compounding ingredients decreased in acetone-chloroform extract, as expected, it was hoped that the curves could be analyzed to give the increasing and decreasing components. This could not be done, as the values obtained were extremely erratic. Even those stocks which should have shown continuous increases in extractables gave very inconsistent results. Inconsistencies were so great, in fact, that no curves could be drawn. Even replicate samples gave results which could hardly be called checks. It was concluded, therefore, that the determination of change in amount of extractables offered no great promise for even a qualitative evaluation of the extent to which vulcanizates had undergone aging.

## COMPARISON OF OXYGEN ABSORPTION WITH AGING DATA

The histograms in Figure 7 show the relative effects of various aging procedures on stocks 2 to 8. The rapid rates of oxygen absorption and physical deterioration during accelerated aging of stock 1 are so pronounced as to make it obviously and unqualifiedly the poorest aging stock of the group. Comparisons, therefore, are necessary only for the remaining seven stocks. Consequently, the data for each stock were compared with the effect on stock 1 under similar conditions. Relative effects on the stocks remained unchanged by this transformation of data.

In general, during bomb aging, each synthetic stock shows a ratio of nearly unity for tensile strength to elongation decay rates. The one exception, stock 4, and the natural rubber, stock 2, both show a decidedly greater effect on tensile strength. It is interesting to note, in comparing stocks 1 and 2 (Tables III and IV), that the addition of an antioxidant increases the ratio of tensile strength to elongation deterioration.

During oven aging, all synthetic stocks show a more pronounced decrease in ultimate elongation than in tensile strength. Stock 2, as during bomb aging, shows a greater effect on tensile strength and an increase of tensile to elongation decay ratio over stock 1.

It is important to consider, at this point, which property provides the best estimate of the degree to which deterioration has occurred in a rubber stock.

TABLE V

RANKING OF STOCKS ACCORDING TO AGING RESISTANCE

| Aging method | Ranking of stocks | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Oxygen absorption rate | 7 | 8 | 5 | – | 6 | 4 | – | 3 | – | 2 |
| Tensile strength | | | | | | | | | | |
| Bomb, rate | 8 | 7 | – | 4 | 5 | 6 | – | 3 | – | 2 |
| Bomb, 96 hours | 7 | – | 8 | 6 | – | 2 | 4 | 5 | – | 3 |
| Oven, rate | 8 | 6 | 4 | 7 | – | 5 | – | 3 | – | 2 |
| Oven, 28 days | 8 | 7 | 4 | 6 | – | 3 | 5 | – | 2 | – |
| Ultimate elongation | | | | | | | | | | |
| Bomb, rate | 8 | 4 | 7 | – | 2 | – | 5 | 6 | – | 3 |
| Bomb, 96 hours | 8 | 7 | – | 2 | 4 | – | 3 | 6 | – | 5 |
| Oven, rate | 4 | 2 | 7 | 6 | – | 8 | – | 3 | 5 | – |
| Oven, 28 days | 4 | 2 | – | 7 | 6 | – | 3 | 8 | – | 5 |

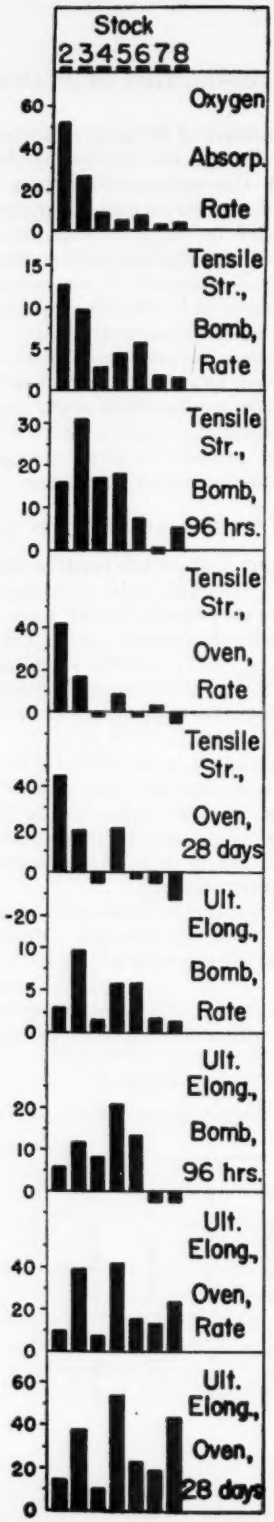



FIG. 7.—Oxygen absorption rate and reduction of physical properties. Expressed as percentage of stock 1.

Also, the question again arises as to what conditions of aging give the best measure of decrease of the property decided upon. Virtually all combinations of property and aging conditions have been used as criteria. Although decrease in tensile strength during several days of aging in the oyxgen bomb is most commonly used for stock evaluation, it is the opinion of the authors that a better measure is provided by the rate of decrease after initial effects have disappeared.

The use of the histograms in Figure 7 for ranking the stocks according to aging resistance makes clear the problems involved. Table V ranks the stocks in groups of nearly equal aging characteristics, as evaluated from Figure 7. The most serious inconsistency is to be found in the decrease in ultimate elongation during oven aging. Many stocks almost completely reversed their positions in rank.

Correlation of rate of oxygen absorption is better with tensile strength than with elongation decay, and, as might be expected, better with bomb than with oven aging results. The correlation of absorption rate with the rate of decay of tensile strength in the bomb is excellent, and is, in fact, closer than the correlation of the latter with the 96-hour test.

## DISCUSSION

The correlation of rate of oxygen absorption with accelerated aging, as measured by decline in physical properties, is attested to by several investigators[14]. Such work had been confined principally to natural rubber and GR-S. Two recent oxidation studies[15] included several synthetic elastomers in the investigation, but, in general, synthetic stocks have been ignored.

Theories of the oxidation of natural rubber[16] are based on the combination with oxygen to form peroxides or hydroperoxides, followed by a rearrangement of the molecule. Deterioration is explained by a further change in the rubber molecule, *i.e.*, chain scission. There is no reason why such a mechanism could not operate in any polymer containing sufficient ethylenic linkages. This criterion is met by all elastomers used in this study, except stock 8. Although Thiokol is not unsaturated, it was included because of interest in its behavior toward oxygen.

Le Bras and Viger[17] have demonstrated that two antioxygenic effects may occur. The usual antioxidant acts by diminishing the extent to which the rubber combines with oxygen, as measured by the oxidizability. However, several compounds, notably mercaptobenzimidazole, provide considerable protection against deterioration without greatly reducing the oxidizability. Such compounds, supposedly, direct the molecular rearrangement to forms which do not terminate in scission of the chain.

## CONCLUSIONS

The information in this paper appears to justify the use of the rate of oxygen absorption as a criterion of aging resistance. It is almost certainly true that where the rate is found to be low, resistance to aging will be high. The evidence of Le Bras and Viger, however, must be considered in the opposite case. With high oxidizabilities and in the absence of positive information regarding compounding ingredients, it would be well to proceed cautiously in drawing conclusions. Here, a standard bomb oxidation would be indicated as a confirmatory test. Since most aging tests are run for comparative purposes

and, often, on substantially similar stocks, the second type of antioxygenic activity seldom needs consideration.

A steady rate of deterioration would be expected to provide a better measure of aging resistance than can be obtained from short-term aging. Initial effects on physical properties are frequently so great that they yield false conclusions. It is understandable, of course, that the time and work required to establish the rate of decay make this method impractical for routine testing. As the rate of oxygen absorption correlates so closely with the rate of loss of tensile strength during oxygen-bomb aging, equivalent information can be obtained in very short periods of time, without the necessity of running whole series of determinations, as would be required to establish a rate of loss of tensile strength.

Although the small amount of oxygen absorbed during a determination may classify the result as an initial rate, the criticism of use of initial physical effects does not apply. Examination of the many long-period oxygen absorption curves reported in the literature reveals no rapid changes or reverses of rate, such as are found with tensile strength curves. Furthermore, the absorption of even relatively small amounts of oxygen is sufficient to change the vulcanizate to a state corresponding to the constant rate portion of the tensile strength curve.

It is concluded, therefore, that, in most cases, measurements of oxygen absorption rates can provide comparative aging information of high reliability and absolute information of at least good validity.

## SUMMARY

The rates of oxygen absorption of two natural and six synthetic-rubber stocks have been measured. In addition, the course of aging in the oxygen bomb and air oven was followed by means of changes in tensile strength and in ultimate elongation of the same eight stocks. Correlation between rates of oxygen absorption and deterioration of physical properties is close enough to justify substitution of a rapid oxygen absorption measurement for longer standard procedures in evaluating the aging characteristics of rubber stocks.

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## REFERENCES

[1] Dufraisse, in "The Chemistry and Technology of Rubber," edited by Davis and Blake, New York, 1937; Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946); RUBBER CHEM. & TECHNOL. **19**, 696 (1946).
[2] Neal and Ottenhoff, *Ind. Eng. Chem.* **36**, 352 (1944); Newton and Scott, *J. Rubber Research* **16**, 37 (1947); RUBBER CHEM. & TECHNOL. **20**, 760 (1947).
[3] Milligan and Shaw, *Proc. Rubber Tech. Conf. London*, 1938, p. 537; RUBBER CHEM. & TECHNOL. **12**, 261 (1939); Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947); RUBBER CHEM. & TECHNOL. **20**, 728 (1947).
[4] Van Amerongen, RUBBER CHEM. & TECHNOL. **19**, 170 (1946).
[5] Williams and Neal, *Ind. Eng. Chem.* **22**, 874 (1930); Milligan and Shaw, *Proc. Rubber Tech. Conf. London*, 1938, p. 537; RUBBER CHEM. & TECHNOL. **12**, 261 (1939); Van Amerongen, RUBBER CHEM. & TECHNOL. **19**, 170 (1946); Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947); RUBBER CHEM. & TECHNOL. **20**, 728 (1947).

[1] Williams and Neal, *Ind. Eng. Chem.* **22**, 874 (1930); Dufraisse, in "The Chemistry and Technology of Rubber," edited by Davis and Blake, New York, 1937; Milligan and Shaw, *Proc. Rubber Tech. Conf. London*, 1938, p. 537; RUBBER CHEM. & TECHNOL. 12, 261 (1939); Morgan and Naunton, *Proc. Rubber Tech. Conf. London*, 1938, p. 599; RUBBER CHEM. & TECHNOL. 12, 235 (1939).
[7] Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947); RUBBER CHEM. & TECHNOL. 20, 728 (1947).
[8] Dufraisse and Le Bras, RUBBER CHEM. & TECHNOL. 12, 568 (1939).
[9] Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947); RUBBER CHEM. & TECHNOL. 21, 398 (1948).
[10] Kemp, Ingmanson, and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1929); RUBBER CHEM. & TECHNOL. 13, 375 (1940).
[11] Van Rossem and Dekker, *Kautschuk* **5**, 13 (1929); *Rubber Age* (N. Y.) **25**, 85, 143 (1929); RUBBER CHEM. & TECHNOL. 2, 341 (1929).
[12] Federal Specification ZZ-R-601a, paragraph III-7b (June 25, 1940).
[13] Federal Specification ZZ-R-601a, paragraph III-7h (June 25, 1940).
[14] Dufraisse and Le Bras, RUBBER CHEM. & TECHNOL. 12, 568 (1939); 13, 604 (1940); Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946); RUBBER CHEM. & TECHNOL. 19, 696 (1946); Albert, Smith, and Gottschalk, *Ind. Eng. Chem.* **40**, 482 (1948).
[15] Van Amerongen, RUBBER CHEM. & TECHNOL. 19, 170 (1946); Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947); RUBBER CHEM. & TECHNOL. 21, 398 (1948).
[16] Farmer and Sundralingam, *J. Chem. Soc.* **1943**, p. 125; RUBBER CHEM. & TECHNOL. 16, 790 (1943); Le Bras, *Rev. gén. caoutchouc* **21**, 243 (1944); RUBBER CHEM. & TECHNOL. 20, 972 (1947).
[17] Le Bras, *Rev. gén. caoutchouc* **21**, 3 (1944); RUBBER CHEM. & TECHNOL. 20, 949 (1947); Le Bras and Viger, *Rev. gén. caoutchouc* **21**, 89 (1944); RUBBER CHEM. & TECHNOL. 20, 962 (1947).

# THE PREPARATION AND PROPERTIES OF HIGHLY PURIFIED RUBBER *

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The preparation of highly purified whole-rubber hydrocarbon has so far been a task which could not be undertaken lightly even in the laboratory. The nitrogenous and other impurities in commercial sheet and crepe rubber are intimately associated with the rubber, and their removal can be effected only by drastic treatment, which may have, and is even likely to have, some effect on the molecular structure of the hydrocarbon. It is, however, relatively simple to obtain, by solution methods, a fraction of the rubber in very pure condition, leaving the impurities in the rest of the material. The fraction of acetone-extracted rubber which first passes into solution in a suitable solvent is almost pure hydrocarbon, except that oxidized rubber tends to pass into solution first. As solution proceeds the residue becomes correspondingly less pure. Subsequent fractions become more and more impure, until there is finally left behind a relatively insoluble gel which contains all the remaining insoluble nonrubber impurities present in the original material. It is well known that this impure gel is tougher than the first fractions and that it vulcanizes more quickly, giving a stronger and harder vulcanizate[1]. The differences in the properties of the fractions may be due to molecular differences in the hydrocarbon, but they may also arise from the relatively large amounts of impurities in the less soluble fractions. For example, dried latex containing all the natural impurities is much harder and less soluble than coagulated sheet or crepe, in which the bulk of the nonrubber substances are eliminated in the aqueous serum. It is unsound, therefore, to compare a pure fraction of rubber hydrocarbon with an impure fraction and to attribute the difference in properties to molecular differences in the hydrocarbon fractions.

The preparation of highly purified whole rubber hydrocarbon from preserved latex instead of from dry rubber has been more successful, but the process is not free from difficulties and may have some effect on the hydrocarbon. The water-soluble nonrubber substances in the aqueous serum can be easily removed by repeated creaming. Unfortunately, the others, mostly on the surface and in the interior of the latex particles, are thrown down with the coagulated rubber. Baker[2] has shown that on the surface of the rubber particles are proteins, fat acids, and sterols. Inside the particles are hydrolyzable substances soluble in alcohol and acetone. Practically all the impurities in rubber except proteins can be removed, therefore, by repeated dilution and recreaming of latex, followed by coagulation and extraction with acetone or alcohol. The proteins amount, however, to about 1 per cent of the dry rubber, and are known to have marked effects on vulcanizing and other properties, so their removal is important for a comparison of the properties of different fractions of highly purified rubber hydrocarbons and also for a comparison of rubber hydrocarbons from different sources. Proteins can be decomposed and made water-soluble by treatment

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with enzymes or alkalies, and one of the best known methods of preparing highly purified whole rubber hydrocarbon is the creaming of warmed latex in the presence of caustic soda, as first described by Pummerer[3]. The method is not easy to carry out, because latex is likely to coagulate long before the successive creaming operations are complete. The alkali fails to remove final traces of nitrogenous substances, amounting to about 0.02 per cent nitrogen on the dry rubber, and there is always the danger that caustic soda may have some effect on the rubber hydrocarbon. Even treatment of fresh latex with dilute ammonia makes the rubber harder and less soluble[4].

A simpler and more reliable method of preparing highly purified rubber hydrocarbon has now been devised, with the additional advantage that it involves no drastic treatment with strong chemical reagents.

Baker[2] has shown that the addition of soap to ammonia-preserved latex causes the protein to be displaced from the surface of rubber particles into the aqueous serum, and the protein can thus be removed by the usual procedure of repeated creaming. It is, therefore, easy to obtain a highly purified latex containing as major impurities only ammonium soaps, together with a little creaming agent and the alcohol-soluble material in the interior of the rubber particles. Dry rubber can be obtained from the purified latex, either by drying or by coagulation with acetic acid. The latter is preferable because fat acids are more soluble in alcohol or in acetone than are the corresponding soaps, and the small quantity of creaming agent (usually ammonia alginate) is mostly removed with the aqueous serum. The fat acids are removed by extraction with alcohol or acetone, preferably in the cold.

The purified rubber still contains about 0.02 per cent nitrogen, which is the same as the amount left in the rubber in Pummerer's alkali process. This nitrogen cannot be removed by enzymes or by heating with alkalies or acids. That it is not part of the rubber hydrocarbon molecule is indicated by the fact that, on fractional solution of the rubber, more is contained in the residue than in the soluble fraction. Moreover, most of it can be removed by dissolving the purified liquid latex in hexane containing ammonium oleate, which solubilizes the water in the latex and enables the rubber in the latex to dissolve completely in the hexane in less than a minute. This solution is much less viscous than normal solutions of rubber in organic solvents. On centrifuging there is a small brown deposit which includes the bulk of the remaining nitrogen and mineral matter. Whereas the dry rubber obtained directly from purified latex contains about 0.02 per cent nitrogen and a similar amount of ash, that obtained from centrifuged, solubilized latex by precipitation with acetone contains less than 0.01 per cent of either. It is considered that rubber obtained from purified latex is about 99.8 per cent pure hydrocarbon after extraction with acetone, whereas that obtained from solubilized centrifuged, purified latex is over 99.9 per cent pure. Most of the technological work subsequently described in the paper has been carried out on rubber which is 99.5 per cent pure, the extra impurities being due to incomplete extraction with cold acetone, which does not easily penetrate into such highly purified material. A suitable mixture of acetone and hexane enables extraction to be more complete.

It is well known that, because of the unsaturated character of the hydrocarbon, rubber is easily oxidized and that some of the natural impurities in latex are very effective retarders of this reaction. It is possible, of course, that the oxidation of rubber commences immediately after the latex leaves the tree, but the mechanical properties of rubber from preserved latex show that oxidation is either very slow or does not lead to marked chain scission.

To conduct all the operations of purification on a reasonably large laboratory scale and in the complete absence of oxygen is extremely difficult, and there is appreciable risk, therefore, that highly purified rubber may be obtained in a partially oxidized condition. That the purified hydrocarbon is softer than crepe from the same latex may be regarded as evidence of this, but it is found that the rubber keeps reasonably well in darkness, and contains approximately no more of the easily dissolved fractions than unpurified crepe. It will be seen also from evidence given later, that the purified rubber has excellent mechanical properties after vulcanization in a suitable mix, whereas deliberately oxidized commercial rubber is definitely inferior. Nevertheless, all operations connected with purification are conducted in darkness.

A convenient method of avoiding oxidation is to add an antioxidant. This is not altogether satisfactory, as antioxidants are reactive materials which may have some effect on the properties of the purified rubber hydrocarbon and on the course of vulcanization. On heating rubber in air, antioxidants not only delay the onset of oxidative softening, but in many cases facilitate preliminary hardening. Of a number of antioxidants tried, pyrogallol appeared to be the most effective in preventing any change in commercial rubber, either hardening or softening. An experiment was, therefore, made in which ammonia-preserved latex was divided into two portions, one of which was purified in the presence of pyrogallol and the other in its absence. The rubber was obtained from the purified latices by drying and also by acetic acid coagulation, making four samples altogether.

TABLE 1

| | 100° C D10 values | | | |
|---|---|---|---|---|
| | Purified without pyrogallol | | Purified in the presence of pyrogallol | |
| | Dried film | Creped coagulum | Dried film | Creped coagulum |
| Not extracted and, therefore, containing ammonium oleate | 92 | 74 | 190 | 168 |
| Extracted with acetone | 157 | 139 | — | — |
| Extracted with acetone and pyrogallol | 237 | 200 | 270 | 256 |

One portion of the samples from the purified latex which had not been treated with pyrogallol was extracted with cold acetone and another portion with a solution of pyrogallol in acetone. The samples from the latex purified in the presence of pyrogallol were extracted with the acetone-pyrogallol mixture alone. The results of parallel-plate plastometer tests on the various samples are shown in Table 1. The usual range of values for commercial sheet and crepe from fresh latex is from 150 to 230 mm./100. For crepe from ammonia-preserved unpurified latex, the plasticity results tend towards higher values in the range.

Before removal of soap, the purified rubber is distinctly soft, but, after the soap has been removed, plasticity values are practically within the range found for commercial sheet. Pyrogallol has an extraordinary toughening effect, perhaps because oxidation is prevented. The toughness of the pyrogallol rubber is not transmitted, however, to the vulcanized product.

So far, technological evidence about the state of oxidation of highly purified rubber prepared in darkness in the presence of air is inconclusive. In any case to study its vulcanizing properties, rubber has to be masticated and therefore

oxidized. To determine the effect of more extensive oxidation than occurs in mastication, acetone-extracted commercial sheet was heated in air at 100° C for 48 hours, and vulcanized in a tire-tread type mix in comparison with extracted sheet. The following results were obtained.

The highly oxidized rubber is much weaker and less resilient than the more normal material. It shows no remarkable difference in resistance to extensive stretch, but is more resistant to small deformations. If highly purified rubber is abnormally oxidized it should, therefore, yield inferior vulcanized material.

TABLE 2

MIX: RUBBER 100, ZINC OXIDE 5, SULFUR 3, STEARIC ACID 4, PINE TAR 3, MERCAPTOBENZOTHIAZOLE 1, MICRONEX BEADS 50
Vulcanized at 134° C

| Property | Oxidized sample | | Unheated sample | |
|---|---|---|---|---|
| | 60 minute cure | 80 minute cure | 60 minute cure | 80 minute cure |
| B.S.I. Hardness (mm./100) | 43 | 40 | 50 | 47 |
| Resilience at 25° C (%) | 44.4 | 43.4 | 52.0 | 51.5 |
| Resilience at 70° C (%) | 50.8 | 49.5 | 58.0 | 58.1 |
| Tensile strength (kg. per sq. cm.) | 150 | 155 | 260 | 230 |
| Modulus at 300% elongation (kg. per sq. cm.) | 104 | 107 | 110 | 118 |
| Elongation at break (%) | 397 | 405 | 523 | 487 |

Vulcanization tests on highly purified rubber not treated with an antioxidant have so far been made in three types of mixes, *viz.*; (1) rubber, sulfur (100:10); (2) mercaptobenzothiazole- skeleton mix, with different proportions of ingredients (sulfur, zinc oxide, mercaptobenzothiazole and stearic acid); and (3) mercaptobenzothiazole mixes loaded with carbon black (Micronex beads). In each mix it displays differences from commercial rubber, but only in the rubber-sulfur mix has it failed to give excellent mechanical properties. Typical results in a rubber-sulfur mix are given in Table 3.

TABLE 3

| Period of vulcanisation (minutes at 148° C) | Tensile strength (kg. per sq. cm.) | | | Modulus at 700% elongation (kg. per sq. cm.) | | |
|---|---|---|---|---|---|---|
| | Preserved latex crepe | Acetone-extracted latex crepe | Purified rubber | Preserved latex crepe | Acetone-extracted latex crepe | Purified rubber |
| 60 | 105 | 78 | 20 | 20 | 13 | 5 |
| 90 | 127 | 95 | 41 | 43 | 21 | 8 |
| 120 | 21 | 80 | 47 | — | 53 | 11 |
| 150 | — | — | 49 | — | — | 15 |
| 180 | — | — | 60 | — | — | 24 |

The highly purified rubber vulcanizes extremely slowly, and the physical effect per unit of combined sulfur is very small. For example, after 150 minutes' cure it is more plastic than elastic when hot, yet contains 2.7 per cent combined sulfur, which is sufficient to give a reasonably strong and well vulcanized product in commercial rubber. In another experiment with a fraction of purified rubber, a sample containing 3.8 per cent combined sulfur was so plastic that it could not be removed from the mold. The observations agree with Bloomfield's conclusions that intermolecular polyisoprene polysulfides

give intramolecular cyclized sulfurated material when heated with free polyisoprene[5]. Nevertheless the quantitatively poor physical effect of combined sulfur in purified rubber, compared with the rate at which reversion occurs on heating well vulcanized rubber, suggests that the intermolecular cross-linking reaction with sulfur may not occur in rubber from which all traces of impurities have been removed.

A possible explanation of the poor results is that oxidation occurs during vulcanization. This is unlikely to be the true explanation, as thoroughly degraded rubber still vulcanizes well, although, of course, it is somewhat weak. It is of interest, however, that highly purified crepe containing pyrogallol gives an appreciably stronger and reasonably vulcanized rubber-sulfur product after vulcanizing for 150 minutes.

The effect of zinc oxide, stearic acid, and carbon black, and combinations of these materials, on the vulcanization of the highly purified rubber-sulfur mix vulcanized for 60 minutes at 148° C is of interest, although the results are not unexpected. They are given in Table 4.

TABLE 4

BASE MIX: PURIFIED RUBBER 100, SULFUR 10

| Adduct | Tensile strength (kg. per sq. cm.) | Modulus at 700% elongation (kg. per sq. cm.) | Vulcanization coefficient |
|---|---|---|---|
| Zinc oxide (5 parts) | 50 | 4 | 2.74 |
| Stearic acid (10 parts) | 12 | 3 | 2.22 |
| Zinc oxide and stearic acid | 38 | 4.5 | 4.65 |
| Carbon black (Micronex beads) (50 parts) | 66 | 42 | 3.74 |
| Carbon black and stearic acid | 80 | 30 | 3.42 |
| Carbon black and zinc oxide | 84 | 45 | 4.54 |
| Carbon black, zinc oxide, and stearic acid | 149 | 97 | 5.39 |

Stearic acid by itself is merely a diluent, and hinders the combination of rubber and sulfur. The reaction is accelerated when zinc oxide is also present, and reaches its maximum value and best physical properties when carbon black is added to the other two ingredients. The evidence that stearic acid helps reinforcement by carbon black is not very strong. Each ingredient has some effect on the chemical reaction between purified rubber and sulfur, and exerts its maximum effect in combination with the other two ingredients. Reinforcement by carbon black is due partly to the effect of the various ingredients on the rate and, therefore, on the manner in which rubber combines with sulfur.

When highly purified rubber was first vulcanized in the A.C.S. mercaptobenzothiazole mix, the products obtained were extraordinarily weak, although they were otherwise well vulcanized. This mix contains 2 parts of stearic acid per 100 parts of rubber. Commercial smoked sheet usually contains 1 per cent of naturally occurring mixed free fat acids. When the stearic acid in the A.C.S. mix was increased to 3 parts to compensate for those not normally present in the purified rubber, the results were little better, but 4 parts gave excellent results and higher proportions still higher tensile strengths. In this respect, the purified Hevea rubber behaves like wild rubber, which also requires a higher proportion of fat acids for optimum results[6]. The most likely explanation is that commercial Hevea rubber contains natural impurities in addition to fat acids which are capable of forming rubber-soluble zinc compounds. In spite of this, purified rubber gives excellent results in a tire-tread mix without additional

fat acid, but tensile strength can be improved still further by adding extra fat acid. In fact, the highest strengths are obtained in the presence of 10 parts of fat acids, which are sufficient to combine with nearly all the zinc oxide present. Zinc oleate alone gives good results, but a reserve of zinc oxide is essential for optimum strength. A comparison of average figures for a series of crepes from ammonia-preserved latex, and from the same latex after purification and extraction of the rubber with acetone containing pyrogallol, is shown in Table 5. The mix for the unpurified crepes consisted of rubber 100, zinc oxide 5, sulfur 3, stearic acid 2, pine tar 3, mercaptobenzothiazole 1, Micronex channel black 50. That for the purified crepes was the same, except that the stearic acid was increased to 4 parts.

The most interesting feature of these results is the improved resilience of purified rubber. This improvement is sufficiently marked to be of practical value if highly purified rubber could be supplied economically on a commercial scale. The impurities which have an adverse effect on resilience are apparently the acetone-soluble materials, since extraction of commercial sheet with acetone has a similar beneficial effect.

TABLE 5

| | | Period of vulcanization at 134° C (minutes) | | | | |
|---|---|---|---|---|---|---|
| | | 20 | 40 | 60 | 80 | 100 |
| Tensile strength (kg. per sq. cm.) | Crepe | 712 | 205 | 205 | 180 | 175 |
| | Purified crepe | 165 | 195 | 215 | 195 | 190 |
| Modulus at 300% elongation (kg. per sq. cm.) | Crepe | 70 | 88 | 109 | 109 | 116 |
| | Purified crepe | 59 | 76 | 99 | 98 | 108 |
| B.S.I. hardness (mm./100) | Crepe | 104 | 60 | 54 | 51 | — |
| | Purified crepe | 119 | 74 | 66 | 62 | — |
| Resilience at 25° C | Crepe | 48.4 | 52.6 | 50.5 | 50.0 | — |
| | Purified crepe | 51.5 | 55.7 | 56.1 | 55.7 | — |
| Resilience at 70° C | Crepe | 49.5 | 56.3 | 56.5 | 56.0 | — |
| | Purified crepe | 51.8 | 61.9 | 62.4 | 62.5 | — |

In this connection it is of interest that the chief African wild rubbers, Funtumia and Landolphia, are markedly inferior in resilience to Hevea, but are still superior to GR-S. Unlike Hevea, acetone extraction of the wild rubbers does not lead to an important improvement in resilience. The nature of the acetone-soluble substances in Hevea rubber which decrease resilience has not yet been studied. Fat acids improve the mechanism of vulcanization in the presence of zinc oxide. Most of the other acetone-soluble substances are, however, likely to be inert, and act as swelling agents, which decrease inter-and intramolecular cohesive forces.

The fact that it is now possible to prepare conveniently on a laboratory scale highly purified rubber enables a comparison to be made of the vulcanizing properties of different fractions of the hydrocarbon, free from complications due to the comparatively large proportion of nitrogenous material in the least soluble fraction. It must be remembered, however, that such traces of impurities as are present tend to be concentrated in the insoluble fraction and may determine the course of vulcanization in a mix containing only rubber and sulfur, and that fractionation by means of solvents, which have to be removed subsequently, is likely to lead to deterioration by oxidation of the rubber unless precautions are

taken which are impractical when a large number of samples have to be examined on a reasonably extensive scale.

The experiments so far carried out show that highly purified rubber dissolves no more easily than crepe from the same but unpurified preserved latex. The sol and gel fractions in some mixes display remarkable differences in the mechanical properties of the corresponding vulcanizates. In the tire-tread mix, both sol and gel rubbers are fairly normal, but gel rubber gives a product with higher resilience than that obtained from either sol or whole rubber. Purified hydrocarbons from different sources also display appreciable differences in resilience after vulcanization in a tread mix, but so far there is no evidence that the differences can be related to the physical properties of the raw rubbers. These are matters which are to be made the subject of future communications.

The work described in this paper is selected from a series of investigations carried out by H. C. Baker, W. G. Wren, and G. T. Verghese. More detailed communications on various aspects of the work are in the course of preparation by these investigators for publication elsewhere.

## SUMMARY

A method is described for obtaining highly purified Hevea rubber, 99.9 per cent pure hydrocarbon, by addition of soap to ammonia-preserved latex to displace the protein from the rubber particle surfaces, followed by repeated creaming, solubilization in hexane, centrifuging, precipitation, and extraction with acetone. Prevention or limitation of oxidation of the pure hydrocarbon was obtained by work in darkness, or by treatment of the latex with pyrogallol and extraction with pyrogallol in acetone. Results are given on the vulcanization behavior of highly purified rubber, showing marked improvement in resilience, while there are remarkable differences in the mechanical properties of vulcanizzates from sol and gel fractions in some mixes.

## REFERENCES

[1] Hauser, Le Beau and Shen, *Rubber Age* (N. Y.) **58**, 59 (1945).
[2] Baker, *Trans. Inst. Rubber Ind.* **16**, 165 (1940).
[3] Pummerer and Pahl, *Ber.* **60**, 2152 (1927).
[4] Roberts, *J. Rubber Research Inst. Malaya* **8**, 179 (1938).
[5] Bloomfield, *J. Polymer Sci.* **1**, 312 (1946).
[6] Hauser and Le Beau, *India Rubber World* **106**, 568 (1943).

# KINETIC ANALYSIS OF RUBBER HALIDES *

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## INTRODUCTION

Elucidation of organic structures by means of kinetic analysis has been less frequently achieved in the study of low-molecular compounds than in polymer chemistry. In general, organic chemists prefer straightforward conclusions from physical measurements to the intricate and sometimes ambiguous information obtainable from kinetic data. In polymers, however, different groups can be united within one macromolecule, and in this case kinetic analysis was until recently the only means of quantitative identification. In the field of vinyl halides it has been applied extensively by Marvel[1] and coworkers, while determination of internal and external double bonds in elastomers has become possible by the work of Kolthoff, Lee, and Mairs[2]. In this study of rubber halides, use is made of the same kinetic principles.

It was known from earlier experience in the field of ring closure reactions[3] that the interaction of organic bases with halides is not catalyzed or inhibited by traces of impurities, and that the reaction shows a typical correlation with (1) the structure of the halide; (2) the structure of the base, and (3) the dielectric and basic properties of the solvent.

A comparison with low molecular models opened the way to distinguish kinetically between: (1) the typical monohalides with allylic, primary, secondary, tertiary, and vinyl halide groups; (2) vicinal dihalides from polyhalides; (3) members of the first group from those of the second group.

An outline of the kinetic method will be given first, and after that the application will be illustrated for the halogenation and hydrohalogenation of natural rubber.

## AN OUTLINE OF KINETIC ANALYSIS

A suitable system for a kinetical separation of two different halogen groups must transform one of the groups rapidly, the other relatively slowly into ionic halogen. As the process of mixing a polymer and a liquid takes at least several minutes, the half-time of the slow reaction must be of the order of hours or days. The choice of a convenient standard temperature depends on these considerations. In general, 100° C was usual for chlorides and 50° C for bromides. Taking a large surplus of the base, the formation of ionic halogen becomes apparently of the first order. All bases are either good solvents or at least swelling agents for the polymers. Inhomogeneity may introduce serious errors through slow diffusion. Nitrobenzene offers advantages as a diluent. It accelerates the reaction with aliphatic bases which have a low dielectric constant.

A survey of reference experiments is given in Figure 1. The expected order of reactivity is found with aliphatic and aromatic bases. Piperidine, the strongest base, is also much more reactive than the weak bases pyridine or

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aniline. Tertiary chlorides do not follow this simple rule; aniline, the base with the highest dielectric constant, is by far the most effective agent in this case.

Figure 1 suggests a number of systems suitable to distinguish between two or more of the halides, *e.g.*, using piperidine, it is seen that the reaction rate for allyl > primary > tertiary > secondary ≫ vinyl chloride; or using aniline, the sequence is allyl > tertiary > primary > secondary ≫ vinyl chloride. Such differences can be enhanced by applying in the first case xylene instead of nitrobenzene as a solvent, or by using in the second case the commercial undiluted base. Moreover, it was found that the allylic compounds have a smaller heat of activation than the tertiary chlorides and show, therefore, a still higher relative reactivity at 70° C.

The next question to answer is in how far such reference compounds can be taken as typical for a halide group in general. It was found that primary alyllic and secondary allylic groups can not be differentiated readily with organic bases, but an additional test with silver nitrate has to be used (see below). Crowding of methyl groups in tertiary chlorides enhances the instability within the limits given in Figure 1. The reactivity of secondary halides decreases in the sequence 2-position > 3-position > cyclic halide. It will be shown later that the similarity between reactivity of reference compound and polymer is very satisfactory.

A more complicated problem is the identification of polyhalides. The following rules, however, hold generally:

1. Reactivity increases in the series aniline < pyridine ≪ piperidine and vicinal dihalide < trihalide ≪ polyhalide.
2. The reaction with piperidine leads mostly to the partial formation of vinyl halides. Interaction with polyhalides occurs with explosive violence, even at 20° C. This phenomenon can be used to differentiate between dihalides and polyhalides.
3. The reaction with aniline at 100° C occurs very slowly; it is, therefore, possible to distinguish allylic and tertiary chlorides from polychlorides at this and lower temperatures, from dihalides and polyhalides, using aniline as a reagent.

## HALOGENATION OF NATURAL RUBBER

Rubber chlorinated in solution either by the action of chlorine or by that of sulfuryl chloride[4] in the presence of nitrogenous impurities has been subjected to kinetic analysis. Only the second method leads to products in which the halogen is homogeneously distributed, but in both cases the chlorine is largely allylic (see Figure 2a). These experiments prove (1) the presence of a very reactive fraction, about 75 per cent of the total chlorine, in products with 20 to 30 per cent chlorine; (2) the gradual decrease of this fraction with increasing chlorine content of the polymer. As the tertiary chloride is much less reactive at 70° in nitrobenzene-aniline, additional experiments under these conditions were necessary to prove the allylic structure of the reactive fraction. It follows from Figure 2b that the tertiary fraction is small.

Under a variety of experimental conditions which have been discussed in part already by Bloomfield[5], chlorine can be added to the double bond of rubber and of gutta-percha. The striking difference in the shape of these curves becomes evident from Figure 3. At about 35 per cent chlorine, the allylic frac-

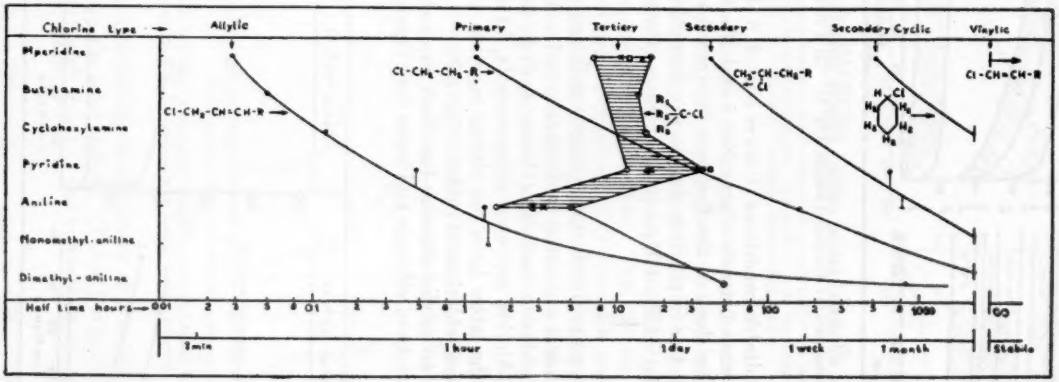


FIG. 1.—Half time of the reaction between monochlorides and organic bases at 100° C; solvent: 4 vols. nitrobenzene + 1 vol. base.

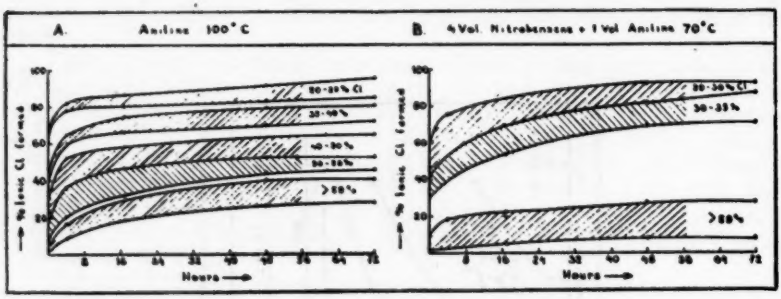


FIG. 2.—Kinetic analysis of chlorinated natural rubber. Chlorine content of rubber variable from 20%—30% to 60% chlorine. Analysis: (1) Undiluted aniline, 100° C. (2) 4 vols. nitrobenzene + 1 vol. aniline, 70° C.

tion disappears under suitable conditions (Curves Nos. 2, 3, 4), while at 46 per cent chlorine the differences between Curve No. 5 and No. 6 are smaller, but not less significant. The slope of the flat part between 5 to 80 hours is not always quite the same; this is possibly due to the formation of the pure dichloride $-CH_2-\underset{\underset{Cl}{|}}{C}(CH_3)-\underset{\underset{Cl}{|}}{CH}-CH_2-$ in some cases (Curves Nos. 4 and 6) and a more complicated polychloride under other conditions (Curves Nos. 2, 3, and 5). This assumption is supported by further experiments with piperidine (see Figure 4). The dichloride fractions (Curves 4, 6) in their reactivity are more related to the dichloride reference substances (a, b) than to the polychlorides (d, c), while the latter have the violent reaction with piperidine[6] in common with the technical chlorinated rubber (Curve 7).

The assumption of an allylic chlorine has been supported by a series of experiments using a variety of solvents and bases (see Figure 5). Only in the

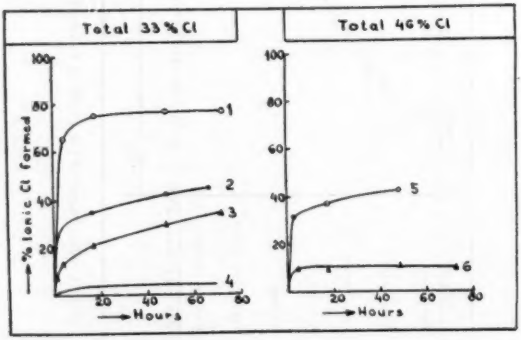


FIG. 3.—Kinetic identification of allylic and addition chlorine. Analysis: Undiluted aniline, 70° C.

| Curve | Method of preparation | % allylic chlorine |
|---|---|---|
| 1 and 5 | Rubber + $SO_2CL_2$ | 72 and 30 |
| 2 | Idem + peroxide | 24 |
| 3 and 6 | Rubber + $C_6H_5ICl_2$ | 12 and 10 |
| 4 | Gutta-percha + $SO_2CL_2$ | 4 |

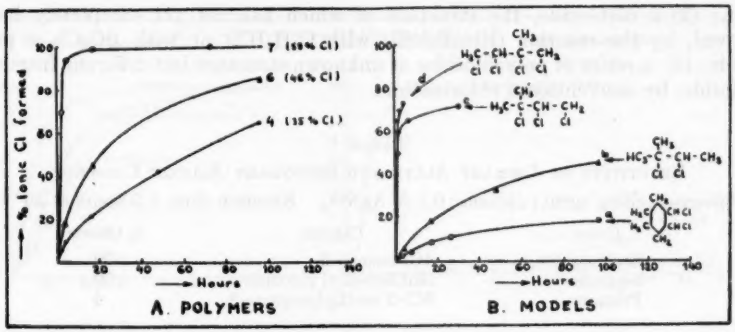


FIG. 4.—Differentiation between dichlorides and polychlorides by their reaction with piperidine (1) with polymers, (2) with reference substances. Analysis: 4 vols. nitrobenzene + 1 vol. piperidine, 100° C. Curves 4 and 6, see Figure 3. Curve 7: Technical chlorinated rubber.

case of the very fast reactions with piperidine, the reference substance is about five times more reactive. This is probably caused by a slow rate of mixing in the beginning. Both with pyridine and aniline, the polymer reacts faster than the reference substance. The theory of Bloomfield[6] and Farmer[7] suggests the occurrence of a secondary allyl chloride. This difference in reactivity between a primary and secondary allyl chloride becomes particularly significant at about 30° C. As at this temperature incomplete swelling may disturb the kinetic test of polymers, use has been made of a test method suitable to show extreme differences between the two type of chlorine, the reaction with silver nitrate (see Table 1).

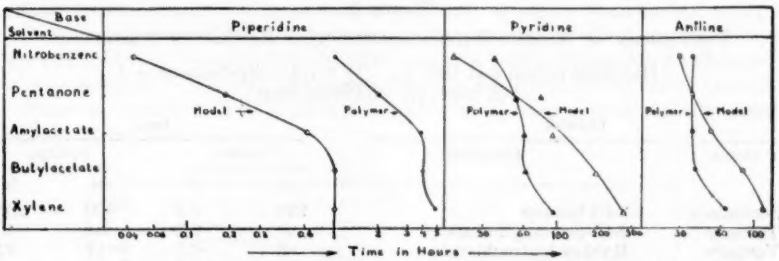


FIG. 5.—A comparison between rubber-allyl chloride and a molecular model ($CH_3 = CH - CH_2Cl$). Reaction at 100° C; half-time in hours; 4 vols. solvent + 1 vol. base.

This astonishing reactivity of secondary allyl chloride is probably linked up with the stability of the allyl radical. Table 1 is in support of the Bloomfield-Farmer theory, although it is not yet possible to distinguish between the two possible structures:

$$-\underset{\displaystyle Cl}{\underset{|}{CH}}-C(CH_3)=CH-CH_2- \quad \text{and} \quad -CH_2-C(CH_3)=\underset{\displaystyle Cl}{\underset{|}{CH}}-CH-$$

Summing up, sufficient kinetic evidence is found for (1) the formation of a secondary allyl chloride, by chlorination under conditions favoring substitu-

tion; (2) a dichloride, the structure of which has not yet completely been proved, by the reaction (Bloomfield) with $C_6H_5ICl_2$ or with $SO_2Cl_2$ + peroxide; (3) a series of polychlorides of unknown structure but different from dichloride, by conventional chlorination.

TABLE 1

REACTIVITY OF PRIMARY ALLYL AND SECONDARY ALLYLIC CHLORIDE

Solvent-swelling agent: dioxane; 0.1 *N* $AgNO_3$. Reaction time, 1.5 hours at 30° C

| Group | Chloride | % Chlorine |
|---|---|---|
| Secondary | 4Cl-hexene-2 | 99 |
| Secondary | Rubber-allyl chloride | 50 |
| Primary | 3Cl-2 methylpropene-2 | 4 |

Very similar tests with bromides at 50° C revealed that bromination leads preponderantly to addition, but exclusively addition-products[5] have not been isolated by the authors. Bromosuccinimide, on the other hand, leads to a preponderance of substitution reactions, although the authors did not succeed in avoiding the simultaneous formation of polybromides.

## HYDROHALOGENATION OF NATURAL RUBBER

In this field of research two different problems have been studied: the course of the addition reaction, and the stability of the resulting halides. All hydrochlorides from natural rubber are kinetically identical independent of the method of preparation. The reactivity is in good agreement with tertiary reference substances and quite different from a secondary chloride (see Table 2).

TABLE 2

COMPARISON OF RUBBER HYDROCHLORIDE WITH REFERENCE SUBSTANCES

Half-time in hours at 100° C. (1) 4 vols. nitrobenzene + 1 vol. base; (2) undiluted base

| Chloride | | Base | | | |
|---|---|---|---|---|---|
| | | Aniline | | Pyridine | |
| Group | Compound | (a) | (b) | (a) | (b) |
| Secondary | 2-Cl-butane | 210 | 9.8 | 400 | 254 |
| Tertiary | 2-Cl-2-methylbutane | 5 | 0.2 | 34 | 40 |
| Tertiary | Rubber hydrochloride | 6 | <1 | 17 | 12 |
| Tertiary | 3-Cl-2, 2, 3-trimethylpentane | 1.5 | 0.05 | 11 | 4 |

A comparison with the reactivity of polyvinyl chloride (PVC) shows a number of interesting features (see Figure 6). The chlorine in PVC is not identical with a secondary monochloride, but corresponds to a 2,4-dichloride. The reaction with piperidine is faster than that of a 2,3-dichloride (Figure 4) or a tertiary chloride (Figure 6). The reaction with aniline and pyridine is much slower than that of the tertiary chloride, and the shape of the curve is typically autocatalytic. The latter fact indicates the intermediate formation of all chlorides, which are finally transformed to polyenes, as is also suggested by the red color of the solution.

The transformation of the system rubber hydrochloride plus base into isorubber and base-hydrochloride is accelerated by a solvent with a high dielectric

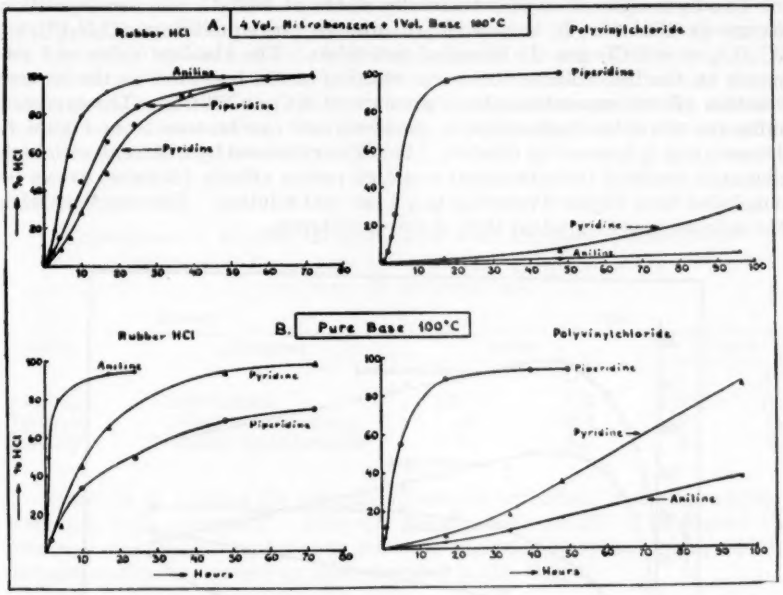


FIG. 6.—A comparison between rubber hydrochloride and polyvinyl chloride. Reaction at 100° C (1) 4 vols. nitrobenzene + 1 vol. base; (2) undiluted base.

constant. The course of the reaction is probably of higher than second order. While a large surplus of the base is necessary to produce the effect illustrated by Figure 6, a few per cent of zinc chloride acts as a true catalyst for the decomposition reaction. This can be observed by the addition of zinc oxide (which of course is transformed into chloride) either to the solution or to the solid polymer on the mill.

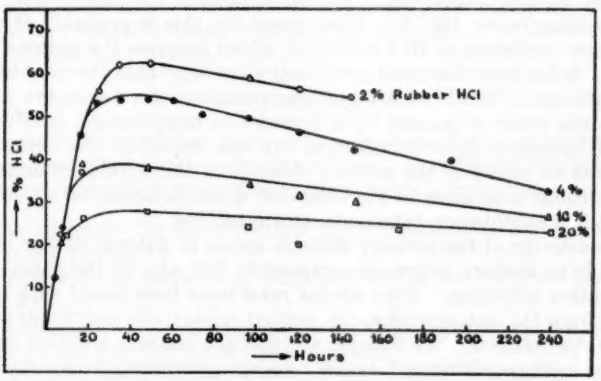


FIG. 7.—Influence of concentration on the equilibrium of dissociation of rubber hydrochloride at 130° C. Solvent: dioxane, closed system.

The hydrochloride is still thermally stable at 100° C, but decomposition occurs at 130° C. It is possible to observe the equilibrium $(C_5H_9Cl)_n \rightleftarrows (C_5H_8)_n + n(HCl)$ gas (I) in sealed test-tubes. The absolute value of I depends on the free volume above the solution in the test-tube, as the reverse reaction affords superatmospheric pressure of HCl at 130° C. The expected influence of rubber hydrochloride concentration can be seen from Figure 7. Dissociation is favored by dilution. It is also enhanced by a solvent with high dielectric constant (nitrobenzene) or a high proton affinity (dioxane) as can be concluded from Figure 8 referring to a 4 per cent solution. Side reactions with the solvent cause a gradual shift of the equilibrium.

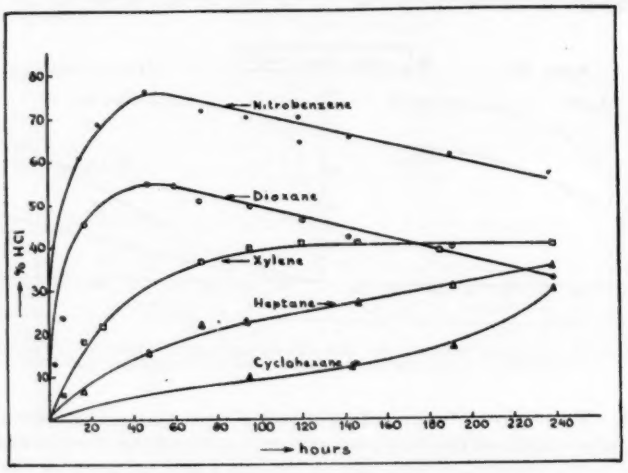


FIG. 8.—Influence of solvent on the rate of dissociation and position of equilibrium of rubber hydrochloride at 130° C.

The equilibrium I in dioxane can be shifted at 130° C to the left side by addition of rubber. However, it proved impossible to cause a shift to the left side by cooling below 100° C. The reason for this is probably the negative temperature coefficient of HCl solubility, which removes the gaseous hydrogen chloride. It has been discussed previously elsewhere[8] that the rate-determining step in hydrogen chloride addition is the formation of a $\pi$-complex compound. Although the latter is favored by a decrease in temperature, it affords also a saturated hydrogen chloride solution. It was hoped at the outset of these experiments to isomerize the tertiary chloride to the secondary under equilibrium conditions analogous to the behavior of butyl bromides[9] at 200° C, but unfortunately equilibrium temperatures are too low.

The reactivity of the tertiary chloride group in natural rubber is not only comparable to tertiary reference compounds, but also to the same structural group in other polymers. Very similar rates have been found with the hydrochlorides from (1) gutta-percha, (2) methyl rubber, (3) polyisoprene, and (4) polymethylpentadiene. As the ease of hydrogen chloride addition seems to be typical for methyl-substituted double bonds in polymers, the absolute value of the chlorine content gives an indication for the degree of cyclization in (1) and (2), the presence of vinyl groups in (3) and (4), and 1, 4-addition in (4).

Addition of hydrogen bromide to natural rubber and to gutta-percha occurs with great ease. Kinetic analysis revealed that about 20 per cent of the resulting bromide is stable, but not at all identical with the secondary bromide. In the presence of air, part of the hydrogen bromide becomes oxidized and acts as brominating agent. Using hydrogen bromide in a hydrogen current, complete hydrobromination occurs. The similarity of the bromide with tertiary reference compounds can be seen from Table 3.

TABLE 3

COMPARISON OF RUBBER HYDROBROMIDE WITH REFERENCE SUBSTANCES

Half-time in hours at 50° C. (1) 4 vols. nitrogenzene + 1 vol. base; (2) undiluted base

| Bromide | | Base | | | |
|---|---|---|---|---|---|
| Group | Compound | Aniline | | Pyridine | |
| | | (1) | (2) | (1) | (2) |
| Secondary | 2-Br-butane | 173 | 4.3 | 127 | 26 |
| Tertiary | 2-Br-2-methylbutane | 4.3 | <0.3 | 10 | 0.4 |
| Tertiary | Rubber hydrobromide | 4 | 0.8 | 5 | 2.5 |

Attempts to prepare the secondary bromide by radical catalyzed addition were not fully successful. Although kinetic tests at 25° C indicated the presence of a secondary bromide fraction, reproducibility was hampered by difficulties already noticed by other workers in this field[10].

## FUTURE ASPECTS

The methods discussed, details of which will be published elsewhere, have been used for about seven years by the authors. They have been applied, not only to the study of reaction mechanism, but also to the development of new technological methods, one of which is discussed by van Veersen[11]. Little use has yet been made of the shape of the curves, which at moderate temperatures reveal more details of halide structure. It is hoped that the heterogenous reaction with KI and $OH'$ will ultimately lead also to intelligible results. Recently infrared analysis has been so much improved[12] that it can be substituted for kinetic tests[13]. It remains to be seen, however, if all quantitative results can be readily obtained from infrared analysis. Probably the methods will be supplementary to each other.

## SUMMARY

A correlation is established between the structure of an organic halide and its rate of reaction with a number of organic bases. Analysis by reaction kinetics, based on this correlation, is applied to the following problems.

(1) Estimation of the allylic fraction in the chlorination and bromination of natural rubber.
(2) Differentiation between a dichloride and a polychloride from natural rubber.
(3) Determination of an equilibrium between natural rubber and hydrochloric acid at 130° C in closed systems.
(4) Identification of tertiary chlorides and bromides in natural rubber and allied polymers.

## ACKNOWLEDGMENT

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## REFERENCES

[1] Marvel, in the "Chemistry of Large Molecules," edited by Burk and Grummitt, Interscience Publishers' New York, **1943**.
[2] Kolthoff, Lee, and Mairs, *J. Polymer Sci.* **2**, 199 (1947).
[3] Salomon, *Helvetica Chim. Acta* **19**, 743 (1936); *Trans. Faraday Soc.* **32**, 153 (1936); **34**, 1311 (1938).
[4] Rubber Stichting, Dutch patent 59,148; Salomon and Koningsberger, *J. Polymer Sci.* **2**, 536 (1947); Bloomfield, *J. Chem. Soc.* **1943**, p. 289; **1944**, p. 114.
[5] Bloomfield, *J. Chem. Soc.* **1943**, p. 289; **1944**, p. 114.
[6] Goldschmidt, German patents 702,172 and 725,848; Jarrijon and Lepetit, *Rev. gén. caoutchouc* **22**, 49 (1945).
[7] Farmer, in "Advances in Colloid Science," Interscience Publishers, New York, **1946**, Vol. 2.
[8] Mayo and Katz, *J. Am. Chem. Soc.* **69**, 1339 (1947); Salomon, *Discussions Faraday Soc.* **2**, 353 (1947).
[9] Huckel and Ackermann, *J. prakt. Chem.* **136**, 15 (1933).
[10] Mayo and Savoy, *J. Am. Chem. Soc.* **69**, 1348 (1947).
[11] Van Veersen, *Proc. Rubber Tech. Conf.* London, **1948**, p. 87.
[12] General Discussion, *Trans. Faraday Soc.* **41**, 171 (1945); Dinsmore and Smith, *Anal. Chem.* **20**, 11 (1948).
[13] Sheppard and Sutherland, *Discussions Faraday Soc.* **2**, 374 (1947).

# REACTION OF BROMINE WITH RUBBER IN AQUEOUS SUSPENSION AND ITS ANALYTICAL USE *

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The rubber hydrocarbon is considered to consist of the combination of an indeterminate number of $C_5H_8$ or isoprene units. In this unit there is a double bond capable of adding two atoms of bromine. This addition takes place with pairs of $C_5H_8$ groups, with formation of the tetrabromide $C_{10}H_{16}Br_4$. Under certain conditions the compound $C_{10}H_{15}Br_5$ is formed, in which case bromine replaces one atom of hydrogen and, at the same time, hydrogen bromide is liberated.

The direct determination of the hydrocarbon of rubber by its transformation into the tetrabromide has been utilized by various investigators. Rubber dissolved in benzene, chloroform, or carbon tetrachloride is treated with a solution of free bromine and carbon tetrachloride. The tetrabromide which is formed is separated and weighed.

The volumetric determination of the rubber hydrocarbon by bromine is generally impaired by the action of the bromine on the solvent and on the impurities which are present in the rubber.

We have tried to study in this work the combination of bromine with rubber in aqueous dispersion, particularly in latex, by an indirect method, based on accepted definitions of the dry rubber content and the total dry residue[1]. The bromine is used in the form of a mixture of bromate and bromide in the presence of acid, and the excess is determined volumetrically. In this way, a bromination factor is obtained, which represents the quantity of bromine consumed per unit of rubber.

Samples of Hevea brasiliensis latex of various concentrations, *viz.*, 30, 50, and 60 per cent, were used, from which aqueous dispersions containing different percentages of rubber were prepared. Equal volumes of these suspensions were treated with bromine for different times under the same conditions of temperature and quantities and concentrations of the reagents. In each case the consumption of bromine was calculated in milligrams of this halogen per milligram of total dry residue and also per milligram of dry rubber content.

When calculated on a basis of the dry rubber content under these conditions, the bromination factor was found to be a function of the time and of the quantity of rubber present in the dispersion, and to be independent of whether the latex is in its natural state or is concentrated.

The results obtained indicate that: (1) the natural components of latex other than the rubber show no appreciable reaction with bromine; (2) bromination continues even after several hours of reaction; and, under the conditions used, the consumption of bromine per unit of rubber is greater than the amount of bromine present in the tetrabromide formed, a phenomenon which can be

* Translated by Alan Davis from the *Anais da Associação Química do Brasil*, Vol. 7, pages 196–199 (1948). This paper was presented before the Division of Analytical Chemistry at the Sixth Congress of the Chemical Society of Brasil, Porto Alegre, February 1947.

explained by derivatives formed by substitution; and (3) the consumption of bromine, under the conditions described, is inversely proportional to the concentration of the dispersion.

Figure 1 shows the variation of the bromination factor with the concentration of the dispersion for a period of 15 minutes of reaction.

Latices of seringueira creamed with jutaí gum and treated with certain preservatives, such as Santobrite, show a smaller consumption of bromine.

To avoid interference of the jutaí gum, latex was concentrated by creaming with the aid of this gum, in the proportion usually employed in practice, and the bromination factor of the resulting latex was determined. The results obtained with latex before and after treatment agreed perfectly.

The use of Santobrite (sodium pentachlorofenate) resulted in the consumption of a smaller amount of bromine. The influence of the concentration of this agent in the latex was not studied, and the mechanism of its action was not investigated.

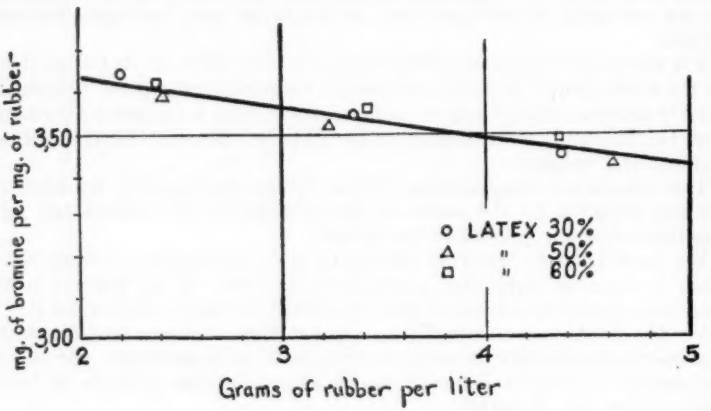


FIG. 1.

In accordance with these results, an analytical procedure was developed for determining the dry rubber content of latices of Hevea brasiliensis not preserved with Santobrite. This study may be extended to other types of latices, for example, that of mangabeira, and the method of determination can be applied to latex of known origin preserved with Santobrite after the corresponding bromination factor has been established.

## ANALYTICAL METHOD

### REAGENTS

(1). —0.2 *N* Solution of potassium bromate and bromide.

Weigh 5.5670 grams of pure dry bromate, dissolve it in distilled water, add 10 grams of potassium bromide and make up the volume to 1000 cc. One cc. of this solution corresponds to 0.01598 gram of bromine.

(2). —15 per cent solution of potassium iodide.

(3). —0.2 *N* Solution of sodium thiosulfate.

### PROCEDURE

(1).—Weight 7 to 8 grams of 30–60 per cent seringueira latex in a weighed filter (weigh by difference) and prepare an aqueous dispersion, making up to 1000 cc.

(2).—Pipet 25 cc. of this dispersion into a 300-cc. flask with a ground stopper; add 50 cc. of the bromate solution and 5 cc. of concentrated hydrochloric acid, close with the stopper, agitate, and allow to stand in darkness for exactly 15 minutes.

(3).—Next add 15 cc. of the iodide solution close with the stopper, agitate, and titrate the excess bromine with the thiosulfate solution, using starch solution as indicator.

(4).—Calculate the rubber content by the relation: $63.9X/(p.f.)$,

where $X$ = cc. of 0.2 $N$ bromate solution consumed
$p$ = weight of the latex
$f$ = bromination factor

### NOTES

1. The factor $f$ is obtained from the graph in Figure 1 corresponding to the concentration of rubber in the dispersion. This latter value, expressed in grams of rubber per liter, is obtained by multiplying the weight of latex by the percentage of dry rubber previously determined by the factor $f = 3.50$.

2. In determining the bromination factor, the relation: $f = 63.9X/(p.B)$ is applied, where $B$ is the precentage of dry rubber in the latex, determined by the method of the American Society for Testing Materials[1].

### RESULTS

Various determinations of rubber in Hevea latices were made by the method which has been described, and the results obtained are shown in the following table.

| Theoretical content (%) | Rubber content | |
|---|---|---|
| | By coagulation (%) | For the bromine (%) |
| 30 | 29.3 | 29.2 |
| 30 | 29.7 | 29.0 |
| 45 | 43.3 | 42.8 |
| 50 | 48.3 | 48.5 |
| Creamed in the laboratory | 52.5 | 52.8 |
| 60 | 59.4 | 59.8 |
| 60* | 57.4 | 54.5 |
| 60* | 59.8 | 57.2 |

* Latices preserved with Santobrite.

In attempts to apply the method to coagulated rubber difficulties were encountered. We had hoped, after solution of the rubber in a suitable solvent, to obtain an aqueous emulsion and thereby to reproduce a latex. However, the most effective solvents which were tried for this purpose were found to be rather sensitive to the action of bromine, as were also the stabilizing and emulsifying agents.

Finally it was decided to use carbon tetrachloride, which, although not the best of rubber solvents, proved inert with respect to bromine. Bentonite was used as a stabilizer in the emulsion.

Several samples of Hevea crepe rubber, obtained by coagulation of concentrated latex by acid, were analyzed by this procedure. Here the absorption of bromine was comparable to that of latex.

## REFERENCE

[1] American Society for Testing Materials, ASTM Standards on Rubber Products, D 640-41T.

# THE HYDROCHLORINATION OF RUBBER IN LATEX *

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The preparation of rubber hydrochloride was first described by Weber[1] in 1900, but it was not before 1934 that rubber hydrochloride, a white powder approximating to the empirical composition $C_5H_9Cl$, received commercial recognition. In that year the Goodyear Rubber Company[2] announced the manufacture of a new transparent, cellophanelike film material made from rubber hydrochloride, named Pliofilm, which has since found widespread use as a packaging material because of properties such as mechanical strength, good flexibility, and good water- and gas-impermeability, due in some measure to partial crystallization[3].

Since 1934 the preparation of rubber hydrochloride has been described in many patents. As starting material, smoked sheet, crepe, balata, gutta-percha, reclaimed rubber, scrap, or sheets from latex can be used. The addition of hydrogen chloride is carried out in solution with the swollen polymer or with solid rubber in liquified or gaseous hydrogen chloride.

Only three processes have been used commercially[4]. (1) Gaseous hydrogen chloride is passed into a solution of masticated rubber until a sufficient quantity has been absorbed, after which the mixture is allowed to "ripen" for a period of time, and the excess of hydrogen chloride then neutralized. This process has been used especially for the preparation of films. (2) Rubber in the form of small cubes is treated with liquified hydrogen chloride under pressure. (3) Thin sheets of milled rubber are suspended in gaseous hydrogen chloride until the desired quantity has been absorbed.

It is obvious that the use of solvents and the complicated apparatus necessary for the handling of liquid hydrogen chloride contribute considerably to production costs.

In this paper we shall show how a careful consideration of the influence of solvents on the rate of reaction of the hydrochlorination of rubber in solution has led to a fundamentally new and simple technical process for the preparation of rubber hydrochloride.

## THE HYDROCHLORINATION OF RUBBER IN SOLUTION

To study the rate of hydrochlorination of rubber in different solvents, we prepared 5 per cent solutions of milled smoked sheet in toluene, toluene-ethyl acetate (2:1 vol.), and toluene-dioxane (2:1 vol.). The hydrochlorination was carried out with 100 cc. of a rubber solution in a jacketed vessel, provided with an outlet in the bottom, which allowed periodical sampling of the reaction mixture. Hydrogen chloride gas was passed through with a constant velocity of 4 liters per hour. The temperature of the reaction mixture was kept constant at 10° C.

* Reprinted from the *Proceedings of the Second Rubber Technology Conference*, London, June 23–25, 1948, pages 87–92. This paper is Communication No. 83 of the Rubber Foundation, Delft.

Samples were taken during the progress of hydrochlorination, precipitated with alcohol, and dried. To remove the last traces of hydrogen chloride, the products were redissolved in toluene and precipitated with alcohol. After drying *in vacuo* the chlorine content was determined either by the Carius method or by heating with aniline[5]. The results are shown in Figure 1.

If we direct our attention to the beginning of the reaction, we observe that, in toluene solution, addition of hydrogen chloride to the rubber begins almost immediately. In toluene-ethyl acetate and toluene-dioxane mixtures, however, the reaction is first delayed for a certain time and then proceeds rapidly. This time lag is due to the fact that the solubility of hydrogen chloride in ethyl acetate and dioxane is much greater than in toluene, and its understanding is the key for our new method.

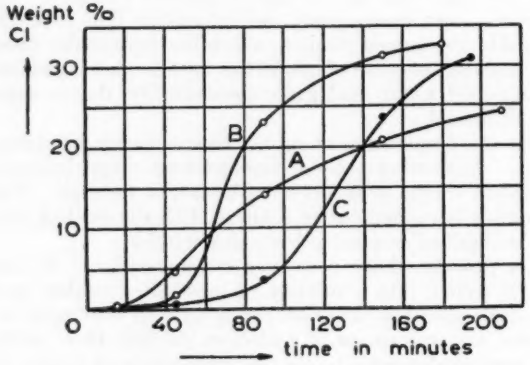
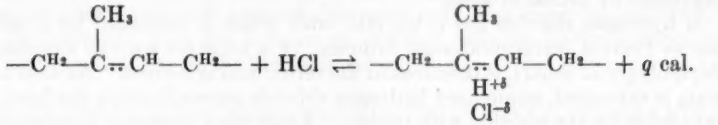



FIG. 1.—The hydrochlorination of rubber in solution. A: rubber in toluene. B: rubber in toluene-ethyl acetate (2:1 vol.). C: rubber in toluene-dioxane (2:1 vol.).

To make clear the kind of interactions which take place between hydrogen chloride and rubber on the one hand and hydrogen chloride and the solvent on the other, we shall discuss the hydrochlorination of rubber from a theoretical point of view. Though we are conscious of the fact that the hydrochlorination of olefins is a complicated reaction[6], we shall give here a more or less simplified scheme which is sufficient for our purpose.

The experiments of Maass and Wright[7] have shown that the hydrochlorination of an olefin takes place through an olefin-hydrogen chloride complex, which is not identical with the final addition product. We may assume that, in the first stage of the reaction between rubber and hydrogen chloride, the formation of a rubber-hydrogen chloride complex is involved. In recent years we have received more insight into these types of complexes by the application of modern electronic theory[8]. The $\pi$-electrons of the double bond of an olefin may be compared with the unshared pair of electrons at the tervalent nitrogen and oxygen atom in ammonia and water and other compounds containing nitrogen or oxygen. Molecules which are capable of donating a pair of electrons, the availability of which is determined by the substituents in the case of olefins and the substituents and electronegativity of the elements nitrogen and oxygen in the case of compounds containing nitrogen or oxygen, can form coordination complexes with acids such as hydrogen chloride. We tentatively

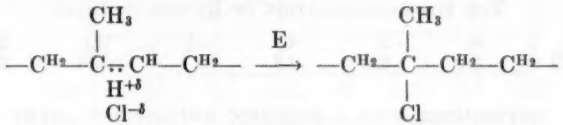
formulate such a complex in the case of rubber as follows:



This coördination complex, the formation of which is accompanied by the evolution of a certain amount of heat ($q$ cal.), exists in equilibrium with rubber and hydrogen chloride. The solubility of hydrogen chloride in dioxane and other ethers depends on the donor properties of the lone pairs at the oxygen atoms. In fact, we have to deal also here with an equilibrium:

$$\text{dioxane} + HCl \rightleftharpoons [\text{dioxane-HCl}] + q_1 \text{ cal.}$$

A solution of rubber in dioxane represents a system of two donors, the double bond in rubber and the oxygen atoms in dioxane, which compete for the available hydrogen chloride molecules. The concentration of the $\pi$-complex compounds depends essentially on the difference $q - q_1$, until the solution is saturated with hydrogen chloride. In fact, the solid complex compound of dioxane and hydrogen chloride, which is formed at $-40°$ C, has been used successfully for the hydrochlorination of olefins and rubber[9]. The third factor influencing the rate of reaction is the activation energy E in the transformation:



E depends strongly on the structure of the olefin and is particularly low in tertiary olefins.

From these considerations it is clear that if hydrogen chloride is passed through a rubber solution, both solvent and rubber molecules compete for hydrogen chloride. The greater the solubility of hydrogen chloride in a solvent, the more the hydrochlorination of rubber is delayed. If, on the other hand, the solvent is saturated with hydrogen chloride, further hydrogen chloride gas can react readily with rubber or another olefin. In ethyl acetate and dioxane the "basic" properties of these solvents are expressed by the occurrence of a time lag. The logical consequence of this line of thought is that rubber in aqueous suspension can also be hydrochlorinated.

## THE HYDROCHLORINATION OF RUBBER IN LATEX[10]

Nature furnishes us by means of the rubber tree with an emulsion of rubber in water, latex. If hydrogen chloride is passed through latex, coagulation takes place, due to the fact that the originally negatively charged latex globules are discharged. It is, however, possible to mix diluted fresh latex with acid without the occurrence of coagulation. Belgrave[11] has shown that the sign of the charge carried by the rubber particles is reversed by acidifying the latex. The positive latex thus obtained is chemically and mechanically unstable. From the work of Blow[12] we know that it is possible to prepare a stabilized positive latex by adding cationic soaps to the rubber emulsion. Alternatively, if non-

ionic emulsifying agents are added to latex, we obtain a latex which cannot be coagulated by means of acids[13].

If hydrogen chloride gas is led into latex which is stabilized by a cationic soap as Fixanol (cetylpyridinium bromide) or a nonionic soap as Emulphor O (oleylpolyglycol ether), it dissolves in the serum and is ionized. As soon as the serum is saturated, nonionized hydrogen chloride passes through the latex, and is available for the reaction with rubber. As the time necessary to saturate the serum depends both on the amount and dry rubber content of the latex and on the velocity with which hydrogen chloride is led in, we began our measurements of the rate of reaction from the moment of saturation in the following experiments:

### EXPERIMENT WITH A CATIONIC EMULSIFYING AGENT

Most of the ammonia was removed from 100 cc. latex (dry rubber content 39 per cent) by a current of air. The latex was added to 40 cc. of water in which 2 grams of Fixanol was dissolved. After mixing thoroughly, hydrogen chloride was led into the stabilized latex. From the moment the serum was saturated with hydrogen chloride, samples were taken at regular intervals; these were coagulated with alcohol, dried, swollen in toluene, and precipitated with alcohol. After drying, the chlorine content was determined. The results are shown in Table 1 and Figure 2, curve A.

TABLE 1

THE HYDROCHLORINATION OF RUBBER IN LATEX

| Time in hrs. | 0 | 3 | 4½ | 9½ | 19½ | 23 | 28 |
|---|---|---|---|---|---|---|---|
| Weight % Cl | 1.1 | 3.4 | 4.1 | 8.1 | 20.6 | 28 | 32.9 |

### EXPERIMENT WITH A NONIONIC EMULSIFYING AGENT

To 100 cc. latex (40 per cent dry rubber content) we added 5 cc. of water in which 1 gram Emulphor-O was dissolved. After passing hydrogen chloride for 48 hours at room temperature, rubber hydrochloride was isolated by adding sodium chloride to the reaction mixture and heating, after which the product (chlorine content 32.7 per cent) was filtered.

Figure 2, curve A, shows that the rate of reaction at normal pressure is slow. This must probably be ascribed to the fact that hydrogen chloride molecules have to diffuse into the latex globules. The diffusion may be the rate-determining factor in the hydrochlorination of rubber in latex under the conditions mentioned.

From a theoretical and technical point of view it was interesting to determine if the rate of reaction could be increased by raising the pressure. To investigate the influence of pressure on the hydrochlorination of rubber in latex we carried out the following experiments. Latex (10 per cent dry rubber content), stabilized with Fixanol, was saturated with hydrogen chloride at 0° C, and sealed in glass tubes (one-third of the volume was filled with latex). The dry rubber content of the latex had to be kept low to obtain sufficient pressure from the hydrogen chloride evolved by heating the latex. A series of sealed tubes was heated at 60° and 90° C, respectively. The initial pressures in the tubes were approximately 3 and 5 atmospheres. To measure the rate of reaction the tubes were opened at different times, the products isolated as usual and the chlorine content determined. The results are shown in Figure 2, curves B and C.

Since further experiments proved that the rate of hydrochlorination of rubber in latex at normal pressure decreases with increasing temperature, it may be concluded that the increase in reaction velocity in the experiments described above is due to the increased pressure.

## PROPERTIES OF RUBBER HYDROCHLORIDE PREPARED FROM LATEX

Microscopical investigation of the diluted latex of rubber hydrochloride from which hydrogen chloride has been removed by dialysis revealed no difference in comparison with diluted ordinary latex.

*x*-Ray investigation of the solid product proved that the material was highly crystalline[14].

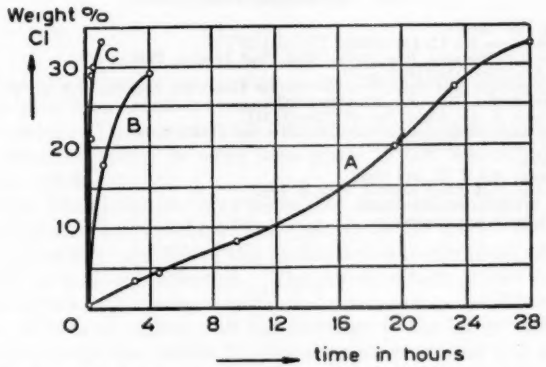



FIG. 2.—The hydrochlorination of rubber in latex. A: 10° C normal pressure. B: 60° C approximately 3 atm. C: 90° C approximately 5 atm.

A striking fact is the high chlorine content of rubber hydrochloride prepared from latex. The theoretical value is 33.94 per cent, but if hydrogen chloride reacts with rubber in solution the maximal chlorine content is only 90 to 95 per cent of this. Starting from latex, we can easily add 98 to 99 per cent hydrogen chloride, showing that under these conditions practically no cyclization or other side reactions occur. This may lead to the assumption that the hydrochlorination of rubber in solution is also void of cyclization. The lower maximum chlorine content of rubber hydrochloride prepared in solution may be explained by the removal of double bonds caused by oxidation or chain fission. We may conclude that the addition of hydrogen chloride to rubber can be used in principle as a means to determine the unsaturation of rubber and probably of its derivatives.

It will be obvious that the process for the preparation of rubber hydrochloride, described in this paper, can be varied in several ways and that the product can be used as a starting material for various technical materials.

## SUMMARY

A careful consideration of the influence of solvents on the hydrochlorination of rubber in solution has led to a fundamentally new technical process for the preparation of rubber hydrochloride.

If hydrogen chloride is passed through latex stabilized with cationic or non-ionic emulsifying agents, rubber hydrochloride is formed. The rate of reaction, which is slow at normal temperature and pressure, can be increased considerably by carrying out the reaction under pressure.

From the fact that rubber hydrochloride prepared from latex has a chlorine content very near the theoretical value, it may be concluded that hydrochlorination of rubber in latex is not accompanied by cyclization.

## ACKNOWLEDGMENT

The author wishes to thank the Rubber Foundation for permitting publication, and G. Salomon for frequent discussions.

## REFERENCES

[1] Weber, *Ber.* **33**, 789 (1900).
[2] *Ind. Eng. Chem., News Ed.* **12**, 444 (1934).
[3] Gehman, Field, and Dinsmore, *Proc. Rubber Tech. Conf.* London, **1938**, p. 961.
[4] *Rubber Age & Synthetics*, May **1947**, p. 79.
[5] Salomon, Koningsberger, and Ultée, *Proc. 2nd Rubber Tech. Conf.* London, **1938**, p. 961.
[6] Mayo and Katz, *J. Am. Chem. Soc.* **69**, 1339 (1947).
[7] Maass and Wright, *J. Am. Chem. Soc.* **46**, 2664 (1924).
[8] Dewar, *J. Chem. Soc.*, **1946**, p. 406; Walsh, *J. Chem. Soc.*, **1947**, p. 98.
[9] U. S. patents 2,285,473 and 2,333,214.
[10] Patent applied for.
[11] Belgrave, *Malayan Agr. J.* **11**, 348 (1923).
[12] Blow, *Proc. Rubber Tech. Conf.* London, **1938**, p. 186.
[13] Hessels, *Chem. Weekblad* **37**, 467 (1940).
[14] Arlman, J. J., private communication.

# ADHESION OF RUBBER AND TEXTILES.* I. PRELIMINARY EVALUATION OF SYNTHETIC RUBBERS IN RUBBER TO FABRIC ADHESION

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## INTRODUCTION

The excellent adhesive properties of natural rubber appear, until fairly recently, to have been taken for granted, particularly when used for coating or plying-up fabrics. There are but few references in the literature to the subject, and little attention seems to have been given to the factors involved in the fabric-rubber bond.

The lack of knowledge on this subject was emphasized during the war when the rubber industry had to adapt itself quickly to the use of GR-S. The relatively poor adhesive properties of this synthetic led to increased attention to the whole subject of tack and adhesion. The adhesive tack of war-time GR-S was so poor that for many purposes it was found necessary to use it mixed with large proportions of natural rubber, but the shortage of the latter material made it essential to find ways and means to reduce the amount used to a minimum. It was with this immediate aim in view that the work to be described was begun. Of necessity the initial investigation was of an *ad hoc* technological nature, and this part of the work is described in Part I of this series of reports. These findings provided a basis on which a more fundamental approach to the subject was planned, designed to determine the precise factors involved in the adhesion of polymers to fabrics. This work is described in Parts II and III[1].

## LITERATURE

A search of the literature has revealed no comprehensive study of fabric to fabric adhesion by means of rubber cements; the only work with a direct bearing on the subject is of Russian origin[2]. Zhukov and Talmud[3] investigated the adhesion due to polybutadiene and natural rubber cements by the method of ply separation of rubberized fabrics. They concluded from stripping tests on a dynamometer that the adhesion of doubled fabrics is mostly a function of the cohesive strength of the binding layer. Krotova[4] observed that the resistance to ply separation of surfaces cemented with either natural rubber or polybutadiene was sensitive to temperature; at low temperatures freezing of the cement layer takes place, and its cohesive strength increases, while its adhesive power remains substantially unaltered. Esman[5], in a paper proposing the revision of the U.S.S.R. Specification OST454 for commercial rubber cements, suggests expressing the adhesion between two strips of cemented fabric in terms of the load ($P$) of separation of the plies in a Scott machine with a speed of separation

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 3, pages 172–221, October 1949.

of 500 mm. per minute, the width of the strip ($b$), and the amount of dried cement per unit area ($G$). From these measurements he develops the expression $K = \frac{P}{bG}$, where $K$ is defined as the specific resistance or bonding capacity. In Specification OST454, the load in kg. per 5 cm. width required to separate the two plies is determined.

Reference to other literature shows that three types of test have been applied to articles bonded together with rubber by one means or another; these are direct separation of two rigid surfaces[6], shear tests[7], and stripping tests[8]. A stripping test was considered to be the most suitable, since it seemed to simulate the manner in which failure of a cemented fabric joint might be expected to occur. As tests of this type were already laid down in Ministry of Aircraft Production Specification K.B.62[9], and Ministry of Supply Specification CS1167[10], it was decided to use one of these tests as a starting point for evaluating cements; accordingly the one in K.B.62 was selected. This Specification covers a nonvulcanizing rubber cement, and the adhesion test consists of sticking together two pieces of double texture ballonet diaphragm fabric, supplied to an M.A.P. Specification, one wider than the other, and, after suitable drying, attaching a dead load to the free end of one piece and noting the amount of stripping in a given time at a temperature not lower than 65° F.

## PRELIMINARY EXPERIMENTS

In the preliminary work, a number of simple solutions of smoked sheet and GR-S in various solvents were prepared, and test-pieces as required for K.B.62 used to compare their adhesive properties, except that amounts of separation in a given time under loads of 4 and 10 pounds were obtained; also from the remainders of the test-pieces one-inch wide strips of combined fabric were cut out and the stripping load was measured at a constant rate of separation of 2 inches per minute, *i.e.*, stripping one inch of combined test-piece. From this preliminary work it seemed that the test most suited to this investigation was the last mentioned, that employing a constant rate of separation.

Further points that were confirmed from these experiments were that the bond strength was very sensitive to temperature[4] and also to the amount of adhesive present[5].

To obtain reproducible results it was clear that the techniques of preparation of solution and spreading would have to be carefully standardized, and that, in testing, account would have to be taken of the temperature and quantity effects. The technique finally evolved is set out in the following section.

## TEST TECHNIQUE

In the preparation of cements the rubbers were, unless otherwise stated, masticated in batches of 400 grams on a 12-inch laboratory mill of friction ratio 1:1.4 with cold rolls and a tight nip. For mixtures of rubber each was milled separately and finally blended on the mill for a short period.

After mastication the stocks were sheeted off thinly and placed immediately in the solvent, allowed to stand about 24 hours, and then stirred in a small paddle mixer. About 3 hours in this mixer for cements of this type usually gives a smooth homogeneous solution.

These solutions were then spread on ballonet diaphragm fabric. To get more than one test-piece from one spreading, pieces about 10 inches wide and

some 24 inches long were used, and the cement was applied by a 12-inch steel straight-edge as spreading knife. To the ends of this knife were attached devices for adjusting the thickness of coat applied. To evaluate the thickness effect for a given cement, an attempt was made to apply a wedge-shaped cement film by uneven adjustment of the spreading blade. Although the application was satisfactory, uneven drying time of the thicker parts of the film made it unsatisfactory, particularly for GR-S cements. The only way to get combination of layers with GR-S was found to be by bringing the solutioned surfaces together before the solvent had fully dried off, due presumably to the poor tack of the GR-S. It was, therefore, decided that a range of separate spreadings would have to be done for each cement, consisting of a minimum of 1, 2, 3, and 4 coats. To compare a range of cements, curves could then be plotted of film thickness against stripping load and, if necessary, the loads read off at one particular thickness. Measurement of the amount of cement present was a difficulty; initially using the K.B.62 technique this was done by weighing the unspread cut-out sections of fabric and the finished test-piece and, by difference, obtaining the weight of dry cement. With the later method this could not be done, as test-pieces were cut from a large doubled sheet after drying. Attempts were therefore made to measure the actual thickness present with a 0.0001 inch dial gauge. The thickness of the fabric was found to be sufficiently uniform to enable a single figure to be taken for the piece used in a single spreading, and by difference the film thickness in individual test-pieces was obtained. With some of the solutions it was subsequently found that negative thickness values were obtained with one-coat spreadings, due to the whole of the cement being used up in filling the gaps between the fibers of the fabric and the rolling treatment given after combining causing a flattening of the fibers.

As poor bond strengths were obtained when so little cement was present, these results were ignored in comparisons, and subsequently two coats and more were used to obtain the data for comparison curves. A modified weighing method could, however, have been used and was tried in addition to the thickness method in one part of the investigation, but since it did not alter the conclusions obtained and took very much longer, it was not generally adopted.

Where more than one coat was given, 5 minutes in a place with free air circulation was allowed for drying between coats and 5 minutes after the final coat. Each piece was then doubled in half, rolled with a 10-pound cylindrical weight 12 times, festooned at room temperature for 24 hours and finally dried at 60° C for 3 hours. Test strips one inch wide were then cut from these, the ends separated by hand, looped back on themselves, and attached to the grips of a resting machine. This consisted of a vertical dynamometer employing a spring balance (0 to 24 pounds) for recording load, and a driven member working at a speed of 2 inches per minute, all enclosed in a wooden cabinet with a glass front. At the base of the cabinet were suitable electric heating elements controlled by a bimetallic thermostat set at 25° C. The cabinet also contained an electric lamp to facilitate reading the balance from outside and a fan to stir the air.

A difficulty in the spreading technique was that some 5 to 10 seconds after spreading a coat of solution small bubbles formed in the film; the trouble seemed to be minimized by spreading very slowly and by using only thin coats. It was mainly associated with the use of double texture fabric, presumably due to air which could not escape through the fabric. This is shown clearly in the stripped back test-piece. in Figure 1.

## EFFECT OF MODIFYING CONDITIONS OF TEST

At the time this work was carried out, emphasis was on obtaining the maximum amount of information about the use of GR-S, so this material was employed as the base of the cements used to investigate the effects of width of test-piece, speed, and temperature of test, as described in the following paragraphs.

*Effect of varying thickness of cement film.*—A range of cements was prepared consisting of (1) 100 parts by weight of smoked sheet, (2) 50 parts smoked sheet and 50 parts GR-S (type CC) and (3) 10 parts smoked sheet, and 90 parts GR-S, all dissolved in crystallizable benzene as 20 per cent by volume

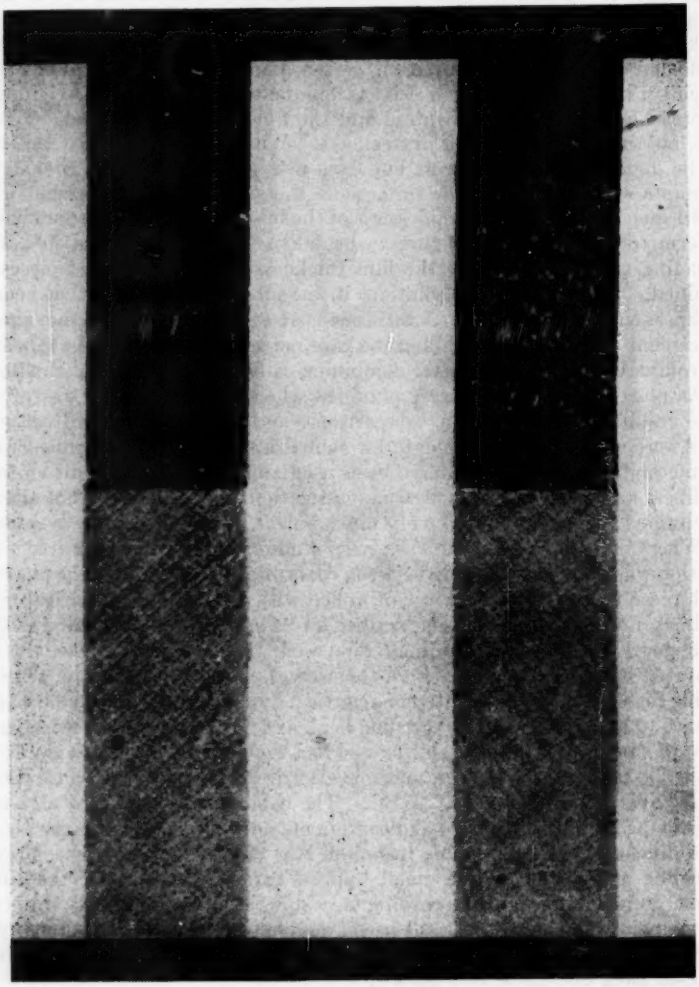

FIG. 1.

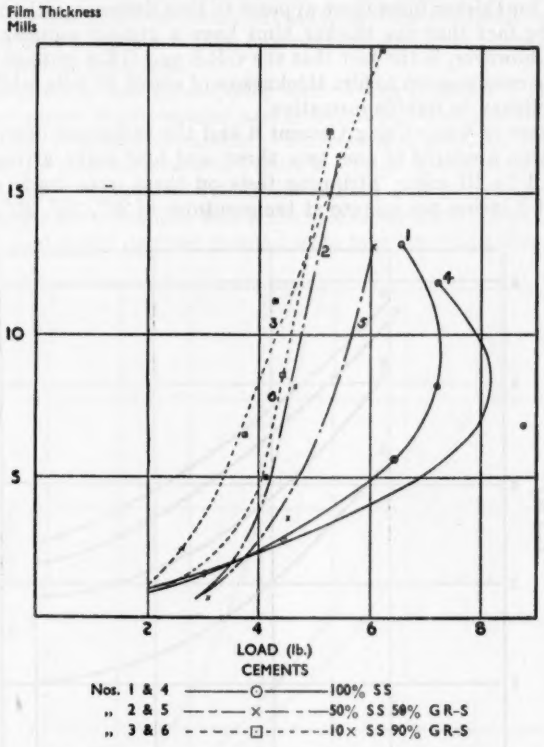


FIG. 2. Relationship between stripping load and cement film.

solutions. The natural rubber and GR-S were masticated for 20 and 5 minutes, respectively.

Curves of stripping load against film thickness were plotted (Figure 2) for these and the following results read off from them:

Cements 1, 2, and 3 were repeated, using fresh rubber, on a separate occasion as 4, 5, and 6 to determine the reproducibility of the whole procedure; the curves for both series are given in Figure 2. The stripping of all the test-pieces, with a very few exceptions, occurred within the cement film, and thus presumably the cohesive strength of these films tested under these conditions is lower than the adhesion of the cement to the fabric.

An examination of the curves in Figure 2 suggests that with 100 per cent smoked sheet, a maximum load is obtained in the region of film thickness 5 to

STRIPPING LOAD OBTAINED WITH 20 PER CENT SOLUTION IN BENZENE

| Cement No. | Rubber as per cent of solids | Load in lb. per in. width for film thickness | |
|---|---|---|---|
| | | 5 mils | 10 mils |
| 1, 4 | 100 Smoked sheet | 6.4 | 7.6 |
| 2, 5 | 50 s.s./50 GR-S | 4.4 | 5.2 |
| 3, 6 | 10 S.S./90 GR-S | 3.7 | 4.4 |

10 mils. and for thicker films there appears to be a decrease, although this may be due to the fact that the thicker films have a greater number of bubbles; against this, however, is the fact that the GR-S and GR-S/rubber mixtures do not show this reversion up to film thicknesses of about 20 mils, while exhibiting the same tendency to bubble formation.

*Temperature of test.*—Using Cement 6 and the technique described above, spreadings were prepared of one, two, three, and four coats, giving film thicknesses from 1 to 10 mils. Stripping tests on these were made at a rate of separation of 2 inches per minute at temperatures of 20°, 25°, 30°, and 35° C.

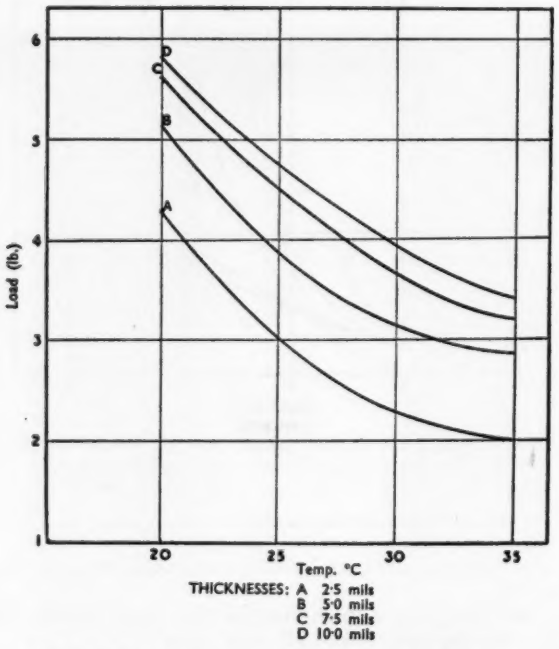


FIG. 3. Effect of temperature on bond strength of GR-S cements.

For each temperature curves were plotted of load against film thickness, and from these curves values at film thicknesses of 2.5, 5, 7.5, and 10 mils were read off. For each thickness curves showing the effect of temperature are given in Figure 3. It seems that the effect of temperature is independent of film thickness, since the curves are parallel, but that the effect of a change of a few degrees is much greater at 20° C than at 35° C.

*Effect of width of test-piece in stripping test.*—Using Cement 6, stripping test-pieces 1, 2, and 3 inches wide were prepared and tested at a temperature of 25° C, and a rate of separation of 2 inches per minute. The results are shown in the following table:

| Load (lb.) at film thickness of | 2 mils | 6 mils | 10 mils |
|---|---|---|---|
| Test-piece 1 inch wide | 0.7 | 1.9 | 2.5 |
| Test-piece 2 inches wide | 2.7 | 4.7 | 5.7 |
| Test-piece 3 inches wide | 4.1 | 6.7 | 8.4 |

The stripping load is not proportional to the width of test-piece for film thicknesses lower than about 7 mils, but as far as these results show it does seem to be above that thickness. The non-proportionality is probably due to a weakening effect of the edges.

*Effect of speed of test in stripping test.*—Using Cement 6 one-inch wide stripping test-pieces were prepared and tested at 25° C at speeds of separation of 2, 4½, 12, and 18 inches per minute. The results of these for film thicknesses of 2.5, 5, and 7.5 mils are shown in Figure 4. In all the work so far described, stripping caused a separation within the cement film and is therefore of the cohesional type; it was thought that if the rate of separation were increased sufficiently the load would increase so much as to take the whole film off the fabric

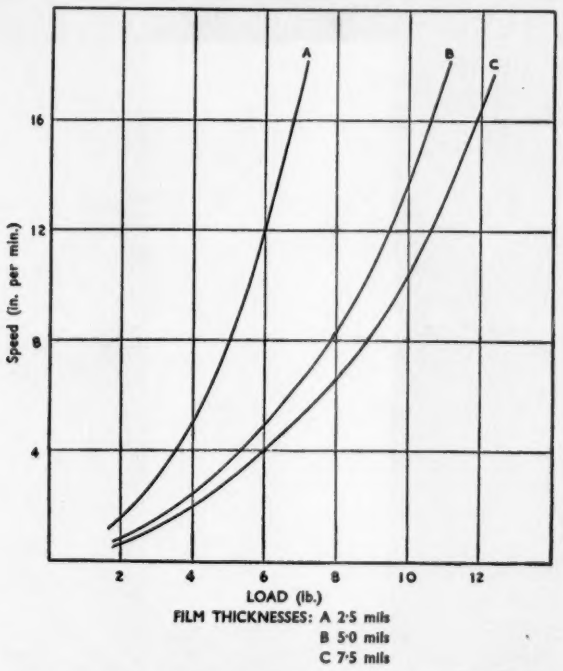


FIG. 4.—Effect of stripping speed on bond strength of GR-S cement.

(adhesional stripping), but this did not occur with the GR-S cement, and presumably still higher rates would be required. Other nonvulcanizing cements prepared from polymers with greater cohesion, such as Hycar OR-15, have shown this adhesional stripping, even at 2 inches per minute. Nearly all vulcanizing cements examined in this work have also shown a much greater tendency to give adhesional rather than cohesional stripping. It seems that, for many nonvulcanizing cements, there is a speed of separation at which the cohesional type of stripping tends to change to the adhesional, and about this speed there is often a tendency to an unstable condition of what might be termed ridge stripping. This appears to be a combination of the two previously mentioned types and manifests itself either as a series of small ridges of polymer,

fairly evenly spaced, and running at right angles to the length of the specimen, or as a series of alternate areas of adhesional and cohesional stripping. Examples of test-pieces that have stripped cohesionally (Figure 5*a*), adhesionally (Figure 5*b*) and exhibited ridge stripping (Figure 6) are shown.

Using natural rubber cements and carrying out the stripping test at 2, 40, and 66 inches a minute, it was found that all tests in the range of film thickness 4 to 10 mils gave cohesional failure at all speeds. At 2 inches per minute, with film thickness about 2 mils, cohesional failure was obtained, whereas, with the same film thickness and speeds of separation of 40 to 66 inches per minute, adhesional or mixture of adhesional and cohesional failure was obtained.

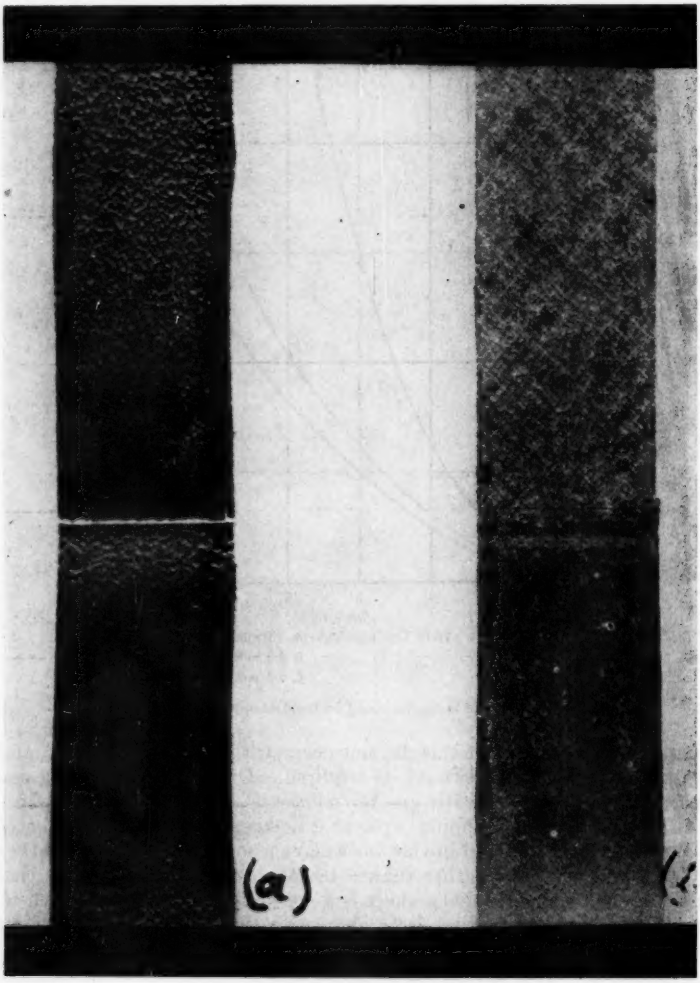


FIG. 5.

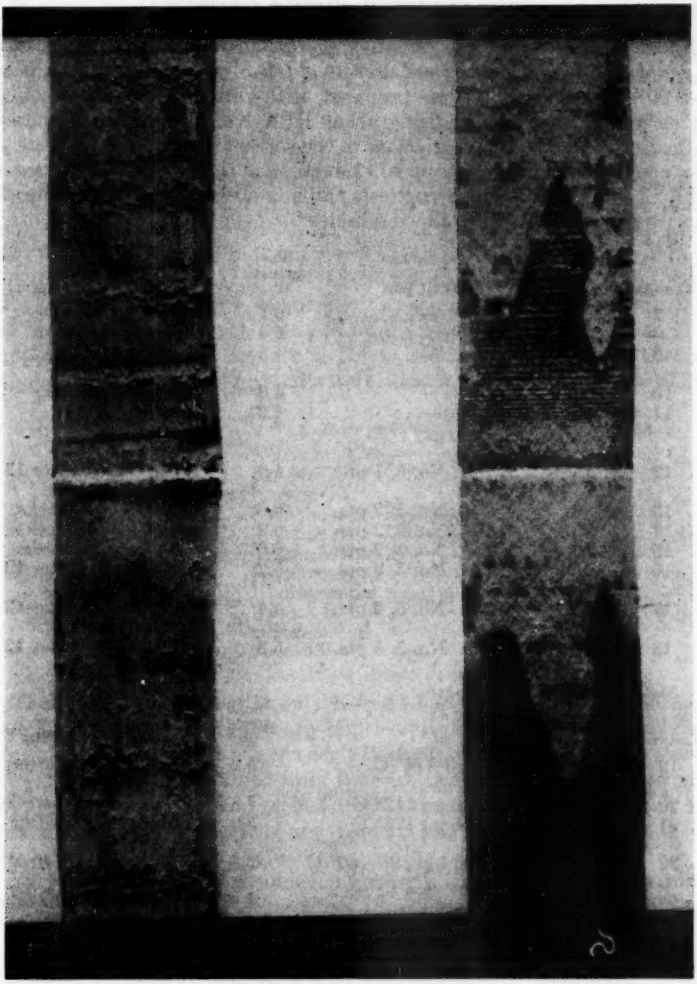

FIG. 6.

Both the effects of speed of stripping and temperature of stripping fit in with the idea that rubbers either at low temperatures or high rates of deformation behave more nearly as rigid solids and consequently have much greater cohesion[4]. If the cement in a test-piece is regarded as a viscous material, the effect of increased speed in causing adhesional separation would be due to the greater stress set up in the cement by deforming it at a high speed. When this stress exceeds the adhesional strength, the film separates from the fabric. The behavior of the vulcanized cements agrees with this, because these have a very high viscosity, and are essentially elastic.

## GR-S NONVULCANIZING CEMENTS

*Effects of mastication time, addition of a peptizing agent during mastication, and changes of solvent on the bond strength of GR-S cements.*—Cements based on GR-S 90/smoked sheet 10 were prepared, with various periods of mastication, varying amounts of the peptizing agent RPA No. 5, and various periods of mastication, and also with variations in the solvent. The cements were stored under cool dark conditions for up to 12 weeks, and their condition was examined weekly. The results of stripping tests and any observations during the storage period are recorded in the following tables:

| Cement | Mastication of GR-S (min.) | Composition: GR-S 90, smoked sheet 10, plus | Bond strength (lb.) | Viscosity or gelling |
|---|---|---|---|---|
| 7 | 5 | — | 6.7 | Gelled in 4 weeks |
| 8 | 10 | — | 5.4 | Gelled in 10 weeks |
| 9 | 15 | — | 4.5 | Very viscous, 12 weeks |
| 10 | 25 | — | 4.0 | Gelled in 10 weeks |
| 11 | 35 | — | 4.2 | Very viscous, 12 weeks |
| 12 | 15 | R.P.A. No. 5, 1 pt. | 4.9 | Little change after 12 weeks |
| 13 | 3 | R.P.A. No. 5, 2 pts. | 6.6 | Gelled after 6 weeks |
| 14 | 5 | R.P.A. No. 5, 2 pts. | 6.2 | Gelled after 9 weeks |
| 15 | 10 | R.P.A. No. 5, 2 pts. | 6.0 | Gelled after 9 weeks |
| 16 | 15 | R.P.A. No. 5, 2 pts. | 5.2 | Little change after 12 weeks |
| 17 | 25 | R.P.A. No. 5, 2 pts. | 4.4 | Little change after 12 weeks |
| 18 | 5 | R.P.A. No. 5, 5 pts. | 5.8 | Little change after 12 weeks |

| Cement | Solvent | Bond strength (lb.) | Viscosity or gelling |
|---|---|---|---|
| 19 | Lotemsol, b.p., 80–114° C | 5.2 | More viscous after 12 weeks |
| 20 | *Solvent No. 2, b.p., 112° C | 4.8 | Gelled after 8 weeks |
| 21 | *Solvent No. 3, b.p., 126° C | 5.0 | More viscous after 12 weeks |
| 22 | Solvent naphtha, b.p., 96–160° C | 5.8 | More viscous after 12 weeks |
| 23 | Pool petrol | 4.4 | Gelled after 9 weeks |
| 24 | Carbon tetrachloride | 4.6 | Gelled after 2 weeks |
| 25 | Benzene | 4.7 | More viscous after 12 weeks |

* Unnitratable solvents of coal tar origin.

Examination of these results shows that bond strength falls rapidly with the first 10 to 15 minutes' mastication, but subsequently very much more slowly. This suggests that a very short mastication gives the best bond, but such solutions are difficult to prepare and gel relatively rapidly on storage. The best compromise under the conditions of the present work was considered to be with a mastication period of 15 minutes, although even this cement gets rather viscous on storage for 12 weeks. R.P.A. No. 5 appears to improve GR-S cements somewhat, both as to strength of bond and in reducing tendency to gel, although even with 2 parts of this it does not seem possible to reduce mastication time below 15 minutes, since cement 15 with GR-S masticated 10 minutes and 2 parts of R.P.A. No. 5 still gels in 9 weeks.

It seems that the solvent with the high boiling fraction (solvent naphtha) gives the best stripping load, presumably due to the retention of some of the high boiling fraction; moreover, this solvent is one which does not cause rapid gelling. Lotemsol and unnitratable solvent No. 3 also appear to be good for GR-S.

*Effects of the addition of resins and tackifiers to nonvulcanizing GR-S cements.*—As it was reported that the German synthetic resin Koresin gave improved bond strength with nonvulcanizing Buna-S cements and also excellent results as a tackifier in dry-mixed Buna-S stocks, it seemed desirable to study the effect of various other resins, and tackifiers for dry-mixed GR-S stocks, in cements. Accordingly a bulk supply of a solution of 90 GR-S/10 smoked sheet in benzene was prepared, with the GR-S masticated 15 minutes and the various resins dissolved in benzene, blended with portions of it in the paddle mixer to give in each case a 20 per cent solution. After spreading a range of coats, stripping at 2 inches per minute at 25° C, and plotting film thickness against stripping load, the following results were obtained at a film thickness of 10 mils:

| Cement No. | Resin or tackifier | Bond strength (lb.) |
|---|---|---|
| 26 | No resin | 4.3 |
| 27 | Koresin-20 | 5.9 |
| 28 | Koresin-40 | 6.3 |
| 29 | Phenolic resin R10825, 40 | 4.5 |
| 30 | Phenolic resin DR7858, 40 | 4.2 |
| 31 | Cumar MH2½, 40 | 6.0 |
| 32 | Wood rosin, 40 | 5.0 |
| 33 | Hydrogenated rosin, 40 | 3.8 |
| 34 | Hytack S | 3.2 |
| 35 | Supatac | 3.8 |
| 36 | Tacaid B | 2.2 |

These results suggest that only Koresin and Cumar resin MH2½ and to a lesser extent, wood rosin, show any improvement over the cement without resin as far as bond strength is concerned. Portions of the cements were stored in a cool dark place and examined from time to time. All the cements containing resins tended to thicken and gel less quickly than the one without resin; of those containing resin, the Koresin and Cumar MH2½ ones tended to gel more quickly than the others.

Further work with inorganic reinforcing fillers both with and without the presence of resins indicated that fillers always tend to reduce the bond strength of nonvulcanizing GR-S cements.

## NATURAL RUBBER NONVULCANIZING CEMENTS

*Effect of grade of natural rubber on bond strength of cements.*—Cements were prepared from eight grades of raw rubber as follows:

MS.1—R.M.A.1 standard quality R.S.S
MS.2—R.M.A.2 R.S.S. or prime estate smoked sheet cuttings
MS.2—R.M.A.3 R.S.S. or prime estate smoked sheet cuttings
MS.3—R.M.A.5 R.S.S. with slight mold
MS.4—R.M.A.1X D19 London standard quality thick first latex crepe
MS.4—R.M.A.2 D20 No. 1 thick "off latex" crepe
MS.5—E24 Clean thin medium brown crepe
MS.5—E31 Brown crepe

200-gram batches of the rubbers were each masticated for nine minutes and dissolved in benzene to give 15 per cent solutions.

Stripping tests were carried out at rates of separation of 2, 40, and 66 inches per minute. At film thicknesses of about 2 mils, stripping was cohesive at the slow speed and adhesive at the faster rates. For thicker films all stripping was cohesive at all rates of separation.

At a stripping rate of 40 inches per minute and a film thickness of 2 mils the following results were obtained:

| Cement No. | Rubber | Bond strength (lb.) |
|---|---|---|
| 37 | MS.1—R.M.A.1 | 5.1 |
| 38 | MS.2—R.M.A.2 | 4.0 |
| 39 | MS.2—R.M.A.3 | 4.6 |
| 40 | MS.3—R.M.A.5 | 5.0 |
| 41 | MS.4—R.M.A.1 X, D19 | 5.0 |
| 42 | MS.4—R.M.A.2, D20 | 5.0 |
| 43 | MS.5—E24 | 5.3 |
| 44 | MS.5—E30 | 4.4 |

These results are quoted only to indicate the general level. A consideration of all the figures obtained at all film thicknesses and at the various rates suggest that there is no significant difference between the adhesive properties of any of the cements made from these different grades of raw natural rubber.

*Effect of addition of resins to nonvulcanizing natural rubber cements.*—Smoked sheet was masticated for 5 minutes and dissolved in crystallizable benzene by steeping in the solvent overnight and finally by agitation in the paddle mixer for a few hours. In the paddle mixer various resins, dissolved in benzene, were added to give a final solution of 15 per cent rubber content (cements 45–50). These were spread on ballonet fabric as previously described to give a range of film thicknesses, after doubling and drying as before, stripping tests at 2 inches per minute and 25° C were carried out, the results being as follows:

| Cement No. | Resin | Film thickness (mils) | Bond strength (lb.) |
|---|---|---|---|
| 45 | None | 0.5 | 5.2 |
| 45 | None | 1.5 | 6.6 |
| 45 | None | 6 | 6.2 |
| 45 | None | 8 | 4.7 |
| 46 | Koresin-40 | 1.5 | 3.7 |
| 47 | Cumar MH2½, 40 | 1.5 | 4.8 |
| 48 | Wood rosin, 40 | 1.5 | 4.0 |
| 49 | Phenolic resin R4036, 40 | 1.5 | 3.8 |
| 50 | Coumarone resin C46, 40 | 1.5 | 4.2 |

As with GR-S cements, the bond strength varies with film thickness. The results with cement 45 (no resin) tended to be variable, owing to the occurrence of the close ridge stripping previously mentioned. None of the resins appear to improve the bond strength as was found to be the case with GR-S, possibly due to the fact that they seem to improve cohesion rather than adhesion. In the case of unvulcanized GR-S cohesion is always considerably lower than adhesion, whereas with natural rubber the two seem to be very nearly the same under the conditions of test employed here (hence the prevalence of ridge stripping) and, accordingly, there is little effect of resins. Test-pieces with these cements were also given 10 days' aging in the Geer oven at 70° C, and were submitted subsequently to the stripping test. Results with the Koresin, Cumar MH2½, and Wood Rosin, all appeared to be similar to those obtained with the control, but

the cements with R4036 and Coumarone C46 appeared to be oxidized to a treacle-like liquid.

## NONVULCANIZING CEMENTS BASED ON BUTADIENE–ACRYLONITRILE COPOLYMERS

The rubbers were masticated in 400 gram batches on the cold mill with tight nip as previously, except that 25 minutes was chosen again because it was known that they were difficult to dissolve unless very well masticated. They were dissolved in a 2:1 by volume mixture of ethyl acetate and ethylene dichloride to give 20 per cent solutions. These were then spread on ballonet fabric to give a range of film thicknesses as before. Results of stripping tests at 2 inches per minute and 25° C on the doubled samples are set out below for a film thickness of 5 mils:

| Cement No. | Polymer | Acrylonitrile content (percent) | Bond strength (lb.) |
|---|---|---|---|
| 51 | Buna-115 | Nil | 2.5 C |
| 52 | Thiokol-RD | 15 | 7.0 A(C) |
| 53 | Butaprene-NF | 22 | 4.2 C |
| 54 | Perbunan (I.G.) | 24.5 | 18 C |
| 55 | Hycar OR-25 | 30 | 14 |
| 56 | Perbunan (Stanco) | 30 | 4.9 C(A) |
| 57 | Hycar OR-15 | 40 | 22 A |

C = Cohesive type of stripping
A = Adhesive type of stripping

The results here are complicated by the occurrence of adhesive stripping in some cases and cohesive in others. With cement No. 52 the very thin films gave cohesive stripping and the rest adhesive, whereas with No. 56 all test-specimens of film thickness about 10 mils, *i.e.*, the thicker film, showed adhesive stripping and all the rest cohesive. At the thickness at which the results are compared each cement gave the indicated type of stripping shown by the majority of its test-pieces. It is clear that the two types of Hycar and the German Perbunan give the greatest bond strength of any polymers yet examined. All these cements showed increasing bond strength with increasing film thickness, both where all test-pieces stripped cohesively and also where they stripped adhesively, although not to the same degree with the latter type. With the thickest films of cement No. 57, *i.e.*, about 9 mils, the fabric began to tear before stripping occurred.

## NONVULCANIZING CEMENTS BASED ON CHLOROPRENE POLYMERS

A range of cements was prepared from Neoprene-CG and Neoprene-GN with and without the addition of the resins found previously to give improved bond strength with GR-S. The Neoprene-GN was masticated for 30 minutes and the Neoprene-CG 15 minutes. Both were then dissolved in benzene and evaluated as previously.

Results of stripping tests at 2 inches per minute and 25° C were as follows:

| Cement No. | Polymer | Resin | Stripping load (lb.) |
|---|---|---|---|
| 58 | Neoprene-GN | Nil | 12.6 A |
| 59 | Neoprene-CG | Nil | 13.5 A |
| 60 | Neoprene-GN | Koresin, 40 | 10 A |
| 61 | Neoprene-GN | Cumar MH2½, 40 | 4 C |
| 62 | Neoprene-CG | Koresin, 40 | 7 A |
| 63 | Neoprene-CG | Cumar MH2½, 40 | 6 C |

A = Stripping, adhesive
C = Stripping, cohesive

It seems that chloroprene polymers make good adhesives for fabric, but they are not improved by the addition of resin, as was found to be the case with GR-S, probably because they have greater inherent cohesion, as demonstrated by the fact that they show adhesive stripping. In cements 61 and 63, the Cumar MH2½ resin appears to have seriously reduced the cohesion of the material. It is interesting to note that accelerated aging at 70° C in an air oven of test-pieces prepared with these cements produced a marked improvement of bond strength of all of them, presumably due to polymerization of the chloroprene and consequent improvement of the cohesion. With this treatment cements 61 and 63 changed over to adhesive stripping.

## VULCANIZING CEMENTS

*GR-S cements vulcanized by the addition of certain isocyanates.*—Information from German sources indicated that improved adhesion had been obtained between Buna rubbers and fabric by the use of small proportions of certain isocyanates, partly, it was stated, by the linking of the ioscyanate chemically to the fabric molecules and partly by the cross-linking of the Buna. To investigate this, a solution of the masticated polymer mixture GR-S 90 parts and smoked sheet 10 parts in benzene was prepared, and 2 parts per 100 of polymer of two different isocyanates added to portions of it (cements Nos. 64, 65, and 66). The isocyanates were added to the cements as a dilute solution in methylene dichloride. These two cements and a control were then spread on ballonet fabric and evaluated as previously. The cement containing methylene diphenylene diisocyanate showed an increase in bond strength, at a film thickness of 10 mils, from 4.4 for the control to 7.2 pounds, and that containing triphenyl

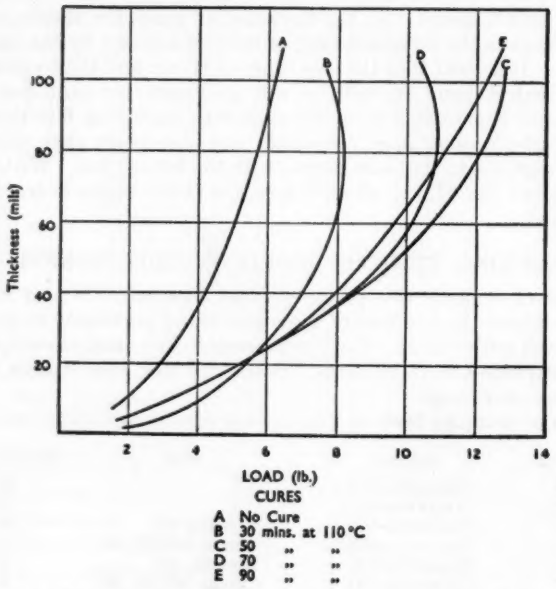


FIG. 7.—Effect of time of vulcanization on bond strength of GR-S cements

isocyanate methane to about 12 pounds. The cement containing the triisocyanate was still usable 24 hours after addition of the isocyanate, but had become very thick after standing 11 days. There was insufficient material available to examine these effects with the cement containing the diisocyanate. Since stripping was cohesive with all these test-pieces, it was presumed that the main improvement was due to cross-linking of the polymer rather than improvement of adhesion to the fabric.

*Heat-vulcanizing GR-S cements.*—A range of cements was prepared to examine the effect of thickness of film on the bond strength of heat-vulcanized GR-S films between two pieces of ballonet fabric. The base stock prepared on the mill was GR-S (Type CC) 100, zinc oxide 3, stearic acid 1, T.M.T. 1.5, and sulfur 2.5. In preparing this the GR-S was premasticated for 15 minutes. Various resins previously tried in nonvulcanizing GR-S cements were added, as solutions in benzene, to the benzene solution of the base stock and to solutions of portions of the base stock to which fillers had been added on the mill. The cements were spread, doubled, and dried as previously and sections of the products vulcanized in an air oven for a range of four periods at 110° C.

The results of stripping tests are set out below for a film thickness of 8 mils at the optimum time of cure as judged by bond strength. Stripping was at 2 inches per minute and 25° C.

| Cement No. | Filler | Resin | Optimum cure (min.) | Load (lb.) | Stripping |
|---|---|---|---|---|---|
| 67 | Nil | Nil | 40* | 9–10 | C(A) |
| 68 | Nil | Koresine, 40 | 40 | 14.4 | A |
| 69 | Nil | Cumar MH2½, 40 | 40 | 13.1 | C |
| 70 | Nil | Coumarone C46, 40 | 40 | 11.6 | A |
| 71 | Nil | Phenolic R10825, 40 resin | 100 | 12.0 | A |
| 72 | Nil | Phenolic DR7858, 40 resin | 40 | 10.7 | A |
| 73 | Zinc oxide 55 | Nil | 45 | 8.8 | A |
| 74 | Zinc oxide 55 | Koresine, 40 | 50 | 12.0 | A |
| 75 | Zinc oxide 55 | Cumar MH2½, 40 | 50 | 13.3 | A |
| 76 | M.T. Black 18 | Nil | 30 | 8.0 | C |
| 77 | M.T.Black 18 | Koresine, 40 | 70 | 10.2 | A |
| 78 | M.T. Black 18 | Cumar MH2½, 40 | 50 | 11.8 | M |
| 79 | E.P.C. Black 18 | Nil | 50 | 10.6 | A |
| 80 | E.P.C. Black 18 | Koresine, 40 | 90 | 14.1 | A |
| 81 | E.P.C. Black 18 | Cumar MH2½, 40 | 70 | 11.6 | A |

* Doubtful figure.

Stripping, A = Adhesive type.
C = Cohesive type.
M = Partly cohesive, partly adhesive.

A consideration of the results in Figure 7 and the table above suggests that, with vulcanized films, increased film thickness still gives increased stripping load, although not to the same extent as with nonvulcanized films. As with nonvulcanizing GR-S films, both Koresine and Cumar MH2½ appear to show an increase in bond strength and, to a lesser extent, coumarone C46 and Phenolic resin R10825. In general, when comparing these results with those of nonculcanizing GR-S cements, the main change is from cohesive to adhesive stripping. It seems, however, that the minimum load to cause adhesive rather than cohesive stripping of a given cement film is progressively reduced by continued

vulcanization, since the majority of test-pieces for overcures in this series showed adhesive stripping. The inclusion of fillers does not appear to improve the bond strength at all.

## SUMMARY

In the bonding of two fabric layers by means of a polymer film, it seems that there are two factors, (1) the adhesion of the fabric to the polymer film, and (2) the inherent cohesion of the film itself. With polymers in which cohesion is normally poorer than adhesion for nonvulcanizing films, *e.g.*, GR-S, stripping under most conditions is of the cohesive type; the stripping load can be increased, in the case of GR-S only, by certain resins with the stripping remaining of the cohesive type. When such polymers are used in vulcanizing cements, stripping becomes of the adhesive type, due presumably to the improved cohesion of the polymer by cross-linking. Further, adhesion appears to be at a maximum for lightly vulcanized films, and gets progressively poorer with further curing.

The importance of control of film thickness in the quantitative evaluation of rubber cements is demonstrated, and a fairly broad picture of the behavior of GR-S in rubber cements is given. It seems that bond strength between two layers of fabric of the same order as with natural rubber can be obtained with GR-S with the addition of suitable resins. The big drawback to its commercial use in cements seems to be the fact that to obtain good bonds it is essential for doubling to be carried out while a fair amount of solvent is still present.

## REFERENCES

[1] This issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[2] Zhukov and Talmud, *Kauchuk i Rezina* 1, No. 5, 43 (1937); Talalay and Magat, "Synthetic Rubber from Alcohol," Interscience Publishers, New York, 1945, p. 274; Esman, *Kauchuk i Rezina* 3, No. 6, 77 (1939); Krotova, *Kauchuk i Rezina* 4, No. 8, 28 (1940).
[3] Zhukov and Talmud, *Kauchuk i Rezina* 1, No. 5, 43 (1937).
[4] Krotova, *Kauchuk i Rezina* 4, No. 8, 28 (1940); Talalay and Magat, "Synthetic Rubber from Alcohol," Interscience Publishers, New York, 1945, p. 274.
[5] Esman, *Kauchuk i Rezina* 3, No. 6, 77 (1939).
[6] Farberov, *J. Rubber Ind. U.S.S.R.* Nos. 8–9, 900 (1936); International Rubber Association, The Hague, "Adhesion Problems in Connection with Rubber Flooring," Rept. Rubber Flooring Research Comm. Propaganda Dept., Intern. Assoc. Rubber and other Cultivations, Netherlands East Indies.
[7] U. S. Army-Navy Aeronautical Specification AN-C-54 (1942); Cement, Rubber.
[8] Ministry of Aircraft Production, Specification K.B. 62, "Rubber Solutions"; Ministry of Supply, Chief Chemical Inspector, Specification C.S. 1167, 1.9.41, "Rubber Solutions, Lead-Free"; Zhukov and Talmud, *Kauchuk i Rezina* 1, No. 5, 43 (1937); Esman, *Kauchuk i Rezina* 3, No. 6, 77 (1939); Krotova, *Kauchuk i Rezina* 4, No. 8, 28 (1940); Talalay and Magat, "Synthetic Rubber from Alcohol," Interscience Publishers, New York, 1945, p. 274.
[9] Ministry of Aircraft Production, Specification K.B. 62, "Rubber Solutions."
[10] Ministry of Supply, Chief Chemical Inspector, Specification C. S. 1167, 1.9.41, "Rubber Solutions, Lead-Free."

# II. FACTORS INFLUENCING THE LOAD REQUIRED TO STRIP RUBBER FROM FABRIC AND FOIL SURFACES

E. M. BORROFF AND W. C. WAKE

## INTRODUCTION

With 2-ply rubber-to-fabric bonds three types of failure were noticed by Hammond and Moakes[1], which they designated adhesive, cohesive, and ridge stripping. The latter two forms arise from inherent weakness of the rubber film compared with the strength of the rubber-fabric adhesion, and may be caused by unusually high adhesive strength just as much as by low cohesion of the rubbery material. In the work to be reported the main interest was the nature

of the bond between the rubber and fabric, and conditions were so arranged that failure was nearly always adhesive. By adhesive failure we mean that the fabric, after test, is completely free from rubber or, if one piece of fabric is only partly free from rubber, then the other piece is complementary to it, so that at no place is rubber left adhering to both faces of the 2-ply test-piece. Where such failure occurs with a fabric containing spun staple, we refer to it as adhesive failure, *i.e.*, failure at the bond interface, even though, as is shown later[2], such failure is connected with fracture of the individual fiber, and is, therefore, strictly associated with cohesive failure of the fabric. This we regard as justified, because the rubber leaves the fabric clean, and such failure is commonly referred to as failure at the bond, as it does, in fact, occur over the region of the interface rather than in the rubber or in the fabric.

In dealing with the complex surface presented by a fabric, some discussion should be made concerning the existence of specific as well as mechanical adhesion. By specific adhesion we mean adhesion that is independent of the form of the surface and can be considered to arise from intermolecular attraction. Mechanical adhesion is well known as that arising from an interlocking or dovetailing of the adhesive into an irregular or porous surface. It may well be that efficient mechanical adhesion cannot occur unless some specific adhesion is also present, since the existence of dovetailing at normal pressures, unless on a very coarse scale, implies the ability of one phase to wet the other. The authors submit some experimental data on the relation between specific and mechanical adhesion in rubber-fabric systems.

*Effect of chemical treatment on the adhesion of a cotton duck to rubber cements.*—Specific adhesion in the sense defined above is obviously sensitive to the chemical nature of the two surfaces brought into contact. To separate any such effect occurring in the presence of mechanical adhesion from the mechanical adhesion itself, a cotton fabric was treated so as to alter the chemical nature of its surface without alteration of the mechanical factor, as (1) the weft and warp naturally remained approximately the same count; (2) the treated yarns themselves showed very similar appearances to the original when examined under a low power microscope. It may be assumed that, to a first approximation, mechanical factors remained unaltered except that the tensile strength of the fabric was found to have been lowered by the treatment. Comparison was thus made of the adhesion of natural rubber, Neoprene-GN, and Hycar OR-25 unvulcanized cements to the fabric as received, and after the following treatments: soda-washed and scoured, nitrated to mono- and dinitrate stages (probably resulting in mixtures of lower and higher nitrates), and acetylated to the diacetate stage. The fabric was a 7½-oz. duck, with warp and weft of 74 threads per in.

The cements were made by dissolving the rubber in suitable solvents after mastication on a cold mill. The general procedure was the same as reported by Hammond and Moakes[1]. Test strips of the fabric were cut on the cross and stripping of these was carried out without reference to the direction of the spun staple. The results are given in Table 1. Those for natural rubber refer to strips 2 inch wide divided by 2, whereas the remainder refer to 1-inch strips; this assumes proportionality between stripping force and width of strip, which does not hold exactly. This inconsistency was the unavoidable result of apparatus contingencies. Also, when the Hycar OR-25 cements were stripped at the constant rates available, only cohesive failure could be obtained. By hanging loads on the strip, results were obtained at constant stress for which, by timing with a stop-watch, a rate of stripping was estimated.

Analysis of variance of the figures in Table 1 shows that, although the differences between rubbers are significant at the 1 per cent level, the individual treatments show no significant change from the untreated material. If, however, all treated materials are grouped together and compared with the untreated material, it does seem that the lowering of strength observed is a real and not a chance effect, although the figures are only at the borderline of significance for a probability of 1 in 20. In this case it is treatment as such that may be responsible and not necessarily the nature of the treatment, and an explanation for this which was realized later is given below.

TABLE I

STRIPPING FORCE IN POUNDS PER INCH WIDTH FOR RUBBER CEMENTS ON CHEMICALLY TREATED FABRICS

(The figures at the headings of the columns show the rate of stripping in inches per minute)

| | Natural rubber | | | Neoprene-GN | | | Hycar OR-25 | | |
|---|---|---|---|---|---|---|---|---|---|
| Fabric | 40 | 66 | 127 | 2 | 40 | 66 | Slow | Medium | Fast |
| Untreated | 7.9 | 9.0 | 10.1 | 13.6 | 21.5 | 20.2 | 12.1 | 18.9 | 22.0 |
| Mean force | | 9.0 | | | 18.4 | | | 17.6 | |
| Sod washed | 7.5 | 6.2 | 7.9 | 13.0 | 19.4 | 20.3 | 17.0 | 18.0 | 18.9 |
| Mean force | | 7.2 | | | 17.6 | | | 18.0 | |
| Nitrated, $N_2$ = 5.5 per cent | 6.4 | 7.5 | 7.7 | 15.0 | 17.4 | 19.1 | — | — | — |
| Mean force | | 7.2 | | | 17.2 | | | | |
| Nitrated, $N_2$ = 7.5 per cent | 6.2 | 6.9 | 7.9 | 10.8 | 17.8 | 18.7 | 18.9 | 20.0 | — |
| Mean force | | 7.1 | | | 15.8 | | | 19.5 | |
| Acetylated, Acetyl = 34 per cent | 6.6 | 8.8 | — | 10.1 | — | — | 14.9 | 16.0 | — |
| Mean force | | 7.7 | | | 10.1 | | | 15.5 | |

All the treatments given above were calculated to alter the surface of the fabric, but only by introducing groups of different nature and therefore of different polarities from a surface already polar by virtue of the hydroxyl groups it contained. An attempt was made, therefore, to change the nature of the surface by giving it a hydrophobic coating. For this purpose the same fabric was treated with a commercial waterproofing agent which was essentially a quaternary ammonium salt having a long hydrocarbon chain, and which becomes attached to the surface with the polar part of the molecule inside and the hydrocarbon chain protecting, as it were, the surface and giving it a waxy coating. In this way the rubber is presented with a nonpolar surface, which, of course, is wetted by the rubber. After preparation, washing and drying, the fabric was spread with rubbers as before; the results of stripping tests are recorded in Table 2.

TABLE 2

STRIPPING FORCE IN POUNDS PER WIDTH FOR COTTON DUCK TREATED WITH A NONPOLAR COATING AND COMPARED WITH UNTREATED FABRIC

(The figures at the headings of the columns show the rate of stripping in inches per minute)

| | Natural rubber | | | Neoprene-GN | | | Hycar OR-25 | |
|---|---|---|---|---|---|---|---|---|
| | 2 | 40 | 66 | 2 | 40 | 66 | Slow | Fast |
| Untreated | 2.7 | 7.7 | 8.6 | 11.4 | 15.4 | 16.1 | 12 | 15 |
| Treated | 3.5 | 7.7 | 8.1 | 8.4 | 11.0 | 10.8 | 10 | 11 |

The thickness of treated and untreated rubber films were strictly comparable, and examination of the figures shows that, although there is no difference with natural rubber, the forces required to strip the two polar rubbers, Neoprene-GN and Hycar-OR, are significantly reduced by some 20 to 30 per cent.

One further experiment was tried with the same batch of cotton duck to indicate any gross effects of moisture on the adhesion. Solvents, as ordinarily available, contain small quantities of water, which is also by no means absent from synthetic rubbers. Fabrics also have a varying and variable moisture content. Some hydrogen bonding might be expected to play a part in the adhesion of materials to cellulose, and if so, the use of wet cements of fabric would interfere by preferential attachment of water molecules at the points where hydrogen bonding is possible. An attempt was made to estimate the water content of the three rubbers used in this investigation, but it was too small to be estimated. One batch of each was therefore masticated and dissolved in a suitable solvent which had been previously dried and distilled. The fabric used was washed, dried at 98° C and kept in a desiccator until used. The control fabric was washed, dried, and allowed to humidify in the ambient atmosphere for 24 hours before use. The results show no significant differences between the dried and undried cements and fabric. It should be noted that, after the cements had dried and the cement surfaces were combined, both dried and undried test-pieces were allowed to condition in a normal atmosphere before testing.

From these experiments with treated cotton duck we may draw the following conclusions. Alteration in the polarity of the cloth does not influence the adhesion by an amount sufficient to be noticeable unless the polarity is substantially reduced by coating the surface with a waxy envelope. In this case the adhesion of the polar rubbers only is affected, being reduced somewhat, but not to the level of natural rubber. The moisture content of fabric and cement at the time of forming the adhesive bond does not seem important. The general weakening of the fabric produced by the chemical treatments does seem to correlate with a reduction in adhesion. This, although not at the time explicable, is in line with the observations reported in Part IV[2]. Reduction in the strength of the fabric by chemical treatment is undoubtedly accompanied by a weakening of the staple fiber from which the yarn is spun. This weakening would, according to ideas later expressed[2], be expected to lower adhesion to rubber.

*Stripping of rubbers from smooth materials.*—In examining the adhesion of rubber materials where the possibility of mechanical keying would be absent, an attempt was made to use, as far as possible, the same stripping test as used with fabrics. The experimental technique adopted in preparing the test-pieces was necessarily altered, since difficulty is experienced in removing solvent from a sandwich of sheet material and, in any case, the rubber and the sheet material might both be soluble although to differing extents, in the solvent used. This might lead to swelling of the film and allow some diffusion to the polymer; although this could not occur with cellulose esters and rubbers, it might with polyethylene and polystyrene, both of which have a limited compatibility with rubbers. The rubber was, therefore, masticated for the same time as when dissolved, but was sheeted and placed between two sheets of the material. The sandwich thus formed was pressed in a vulcanizing press at 100° C for 10 minutes, allowed to cool to 50° C before removal, cooled to room temperature, and the adhesion tested by stripping after a conditioning period of 24 hours.

Sheet materials were used, both as received and extracted by suitable solvent to remove plasticizers snd humectants, but the altered flexibility after extraction probably accounts for some if not all of the difference in the load required to strip the material from the rubber between extracted and unextracted. An alternative was tried in some cases, in which solution spreading of the rubber was employed, but instead of a sandwich of the sheet material, cotton duck was pressed onto the cement, the solvent drying out through the fabric; these were not satisfactory, since no adhesion was found in several cases where the corresponding heat bonding showed a definite load required to strip. Faulty technique, *e.g.*, failure to remove solvent, might easily give rise to conditions leading to no adhesion, but could scarcely cause exhibition of this property where it does not exist. Results from the solution spread, cements were therefore discarded.

Stripping was attempted at three or four rates, but in many experiments no load was recorded. Zero figures have been ignored in considering the results, except where all rates of stripping gave zero load, even on complete replication of the experiment. The results obtained are indicated in Table 3.

TABLE 3

ADHESION TO SHEET MATERIALS

| | Sheet material | Natural rubber | Polychloroprene | Butadiene-acrylonitrile copolymer (Hycar-OR) | Butadiene-methyl-methacrylate copolymer |
|---|---|---|---|---|---|
| Increasing polarity of sheet material ↓ | Polyethylene (extracted and unextracted) | NL | B | NL | NL |
| | Polystyrene (unextracted) | A | D | D | C |
| | Rubber hydrochloride (unextracted) | B | D | D | — |
| | Viscose (cellophane): | | | | |
| | Unextracted | B | D | A | A |
| | Extracted | A | C | D | — |
| | Cellulose acetate Clarofoil): | | | | |
| | Unextracted | B | C | D | A |
| | Extracted* | — | C | C | D |

* Results available for solution bonded samples only.
NL = No load.
A = Slight adhesion, stripping load much less than 1 lb. per in.
B = Stripping load of about 1 lb. per in.
C = Stripping load greater than 1 lb. per in.
D = Stripping load greater than strength of the foil used.

The results cannot be regarded as conclusive, but they indicate the following trends. The adhesion due to electronic interaction (the ordinary van der Waals forces) is smaller than can be assessed by the technique used, *i.e.*, smaller than the experimental limit, and consequently no load was recorded as required to strip natural rubber from the completely saturated polyethylene. With the exception of polychloroprene, rubbers containing permanent dipoles can also be stripped off polyethylene at zero load. If the rubbers are combined with polystyrene, which possesses no permanent dipole but is polarizable by other permanent dipoles, only slight adhesion is found with the nonpolar natural rubber, but good adhesion with polar rubbers. Cellulose and cellulose acetate, both of which possess permanent dipoles (although some in cellulose itself will be nulli-

fied by hydrogen bonding), can show, under favorable conditions, some adhesion to natural rubber, the double bond of which would be polarized by the close approach of a permanent dipole.

It is to be expected, therefore, that differences in the magnitude of the specific adhesion exist, according to whether the two surfaces possess dipoles or one possesses dipoles and the other is polarizable or whether they are nonpolarizable and the only force field around the molecules composing the surface is that due to electronic interaction. This would be in line with the observations of others on the adhesion of different materials. This does not deny the possibility of adhesion between nonpolar surfaces but it does require that polar and polarizable materials exhibit adhesion of a higher order than nonpolarizable materials, and it is this higher order that we call good adhesion.

*Relative importance of specific and mechanical factors.*—It appears from this examination of bonding to sheet materials that, although adhesion can obviously exist between two hydrocarbon surfaces, it only becomes appreciable if one surface is polar and the other polarizable. The yarn from which most fabrics are constructed is essentially polar even though, as in nylon, the surface polarity is much reduced by the hydrogen bonding occurring with surface crystallization—a consequence of cold drawing the fibers. Reduction of this polarity by providing a hydrophobic coating does seem to influence the adhesion of the polar rubbers somewhat (see Table 2). If this waxy coating acted merely as a lubricant to assist mechanical slippage, the same reduction would be expected for natural as for the synthetic (polar) rubbers, but this is not so. Such a coating is unlikely to be perfect and, in any case, some adhesion would result from the van der Waals forces of the hydrocarbon; hence we need not be surprised that adhesion is only reduced and not prevented. The small amount of this reduction and the failure to distinguish difference in adhesion to fabrics which have the same mechanical features but different polarities (Table 1) suggests that mechanical factors are far more important than specific factors; it thus remains to demonstrate which are important features of the factors styled mechanical and how they determine the strength of the bond.

*Nature of the mechanical factor in adhesion.*—Mechanical factors may include those peculiar to the yarn and those peculiar to the weave, both may be important and both might interact in different ways with rubbers of differing mechanical properties, *i.e.*, differing modulus. Factors peculiar to the yarn can be largely eliminated by using continuous filament even if monofils are not practicable and, of the materials available, nylon is the most suitable since its cross-section, unlike regenerated cellulose, acetate silk, and so on, is circular.

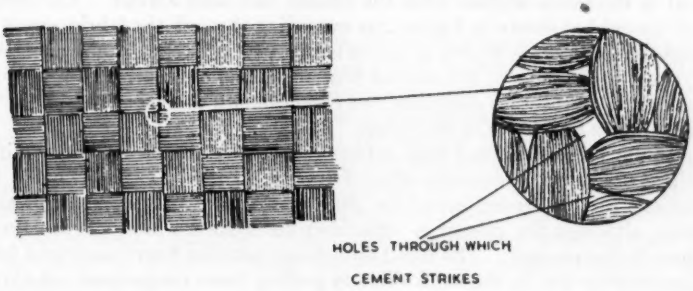


FIG. 1.

Two nylon fabrics were available, both woven from continuous filament fibers so that the fabrics represented as it were, an intermediate stage between the cotton fabric and the smooth film materials if considered from a mechanical point of view. The threads of the material are quite smooth, but there is the possibility of mechanical adhesion by penetration through the fabric at the interstices or of the threads themselves. The two types of fabric used are referred to as light and heavy. The former consisted of a simple weave of twisted monofils of 105 warp and 130 weft per inch, while in the latter the warp of 29 and weft of 28 per in. both consisted of multifiber filaments, untwisted, each of a large number of separate filaments of the same count. The structure of the heavy fabric is illustrated in Figure 1.

The fabrics and cement layers were examined before and after stripping, and it was found that the cement had struck through the heavy nylon with each of the rubbers. The detailed findings are as follows:

(1) *Light fabric.*—Pattern of weave shown on the cement film with evidence of penetration into but not through the fabric. Fabric surface clean on one side or other of the cement film, *i.e.*, the stripping was adhesive, the cement remaining in patches on one piece of fabric or the other, the complementary surface in each case remaining clean.

(2) *Heavy fabric.*—In this case, the cement had, at each crossing of the fiber bundles, penetrated right through the fabric and spread slightly on the glass on which the fabric was placed during spreading and drying.

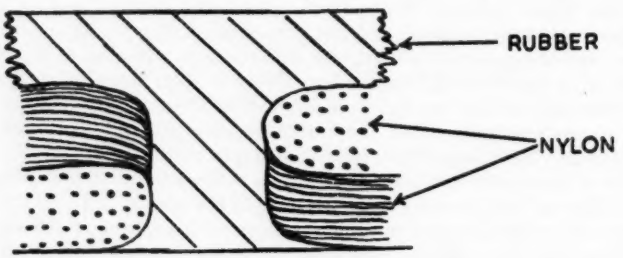


FIG 2.

Figure 1 illustrates the weave of this fabric, and Figure 2 shows a section normal to the fabric surface after the cement had been spread. The penetration of the rubber shown in Figure 2 as extending through the fabric occurs only through the interstices shown in the enlarged part of Figure 1. During stripping, these projections to the cement film are pulled out, since, after stripping, the holes in the fabric are clean and free from cement, even though some cement persists on the underside of the fabric.

Irregular projections and torn rubber can be seen on the rubber film if it is examined under the microscope after stripping. In vulcanized cements, these projections are preserved intact on the cement film, but with unvulcanized cements, although the rubber is withdrawn through the fabric, it is deformed and torn in the process. The small differences between heavy and light fabrics are presumably due to the work done in pulling these projections out through the fabric. The fact that the differences are so small suggests that the coarse

type of keying which these projections represent is not a significant factor in adhesion.

The loads required to strip both unvulcanized and vulcanized rubbers from these two fabrics are given in Table 4, together with the corresponding loads for a 7½-oz. cotton duck for purposes of comparison.

TABLE 4

STRIPPING FORCE IN POUNDS PER WIDTH FOR RUBBER CEMENTS ON NYLON AND COTTON

| | Natural rubber | | | Polychloroprene | | | Butadiene acrylonitrile copolymer (Hycar OR-25) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Light nylon | Heavy nylon | Cotton duck | Light nylon | Heavy nylon | Cotton duck | Light nylon | Heavy nylon | Cotton duck |
| Unvulcanized | 6.2 | 8.1 | 9.0 | 7.9 | 11.2 | 18.5 | 20.3 | 26.2 | 17.6 |
| Self-vulcanized at room temperature for 21 days | 2.9 | 3.5 | 10.6 | 4.6 | 3.5 | 14.5 | 4.4 | 4.8 | 11.9 |
| Vulcanized in press for 5 mins. at 105° C | 3.5 | 6.2 | 15.6 | 6.4 | 7.3 | 38.3 | 6.2 | 5.3 | 17.6 |

The figures quoted are the means for two rates of stripping, since no trend was apparent in the figures. The degree of swelling of the vulcanized rubber in benzene showed that the rubber of the press-vulcanized test pieces were more cross-linked than that vulcanized at room temperature. The self-vulcanizing mix was used for the press-cured experiments, so the details given in the next paragraph refer to both series.

The rubbers for these cements were initially masticated with cold rolls and a tight nip, in 400-gram batches, the batches being then divided into two parts for compounding as given in Table 5.

TABLE 5

| Natural rubber *9 min. mastication* | A | B | Neoprene-GN *30 min. mastication* | A | B | Hycar OR-25 *20 min. mastication* | A | B |
|---|---|---|---|---|---|---|---|---|
| Natural rubber | 100 | 100 | Neoprene-GN | 100 | 100 | Hycar OR-25 | 100 | 100 |
| Zinc oxide | 10 | — | Triethanolamine | 0.75 | — | Stearic acid | 1 | 1 |
| Sulfur | 8 | — | Zinc oxide | 5 | — | Zinc oxide | 5 | 5 |
| ZIX | — | 4 | Catechol | — | 2 | Sulfur | — | 4 |
| | | | Salicylic acid | — | 4 | ZIX | 3 | — |
| | | | | | | ZDC | 3 | — |

After compounding, each mixing was refined by passing through a tight nip 5 times. The mixings were then cut up and placed in suitable solvents, benzene for the natural rubber and Neoprene and a 2 to 1 mixture of ethyl acetate and ethylene dichloride for the Hycar. After approximately 24 hours, each solution was transferred to a mechanical mixer and stirred for 3 hours. Just before spreading, equal volumes of the appropriate solutions were stirred together for 30 minutes. Thin films of the resulting solutions were spread, and when the solvent had substantially evaporated, each piece of cloth was doubled over and rolled with a 10-lb. cylindrical roller. 8 × 1 inch strips were cut from each sheet and allowed to cure at room temperature, the cement thickness being about 0.007–0.008 inch.

In the absence of measurements of the total surface area involved it is difficult to draw quantitative conclusions, but the stripping loads for the unvulcanized rubbers from nylon are not very much greater than those required to strip from (for example) cellophane or cellulose acetate foil, suggesting that what increase there is is due only to the increased surface area provided by the fiber bundles and the nature of the weave. This, in turn, suggests that the very much greater adhesion to cotton is connected either with the projecting ends of the staple fibers or with the fiber irregularity. The nature of the weave is of some importance in providing an increased surface area for adhesion and providing opportunities for some slight keying. This last is more pronounced where the cement can strike through. Keying of the type mentioned is not the only or even the most important factor in securing the good adhesion of rubber to cotton, for this seems to be connected with the fact that cotton is an irregular fiber needing to be spun.

SUMMARY

By means of experiments with chemically treated fabrics in which the mechanical factor is left unchanged and other experiments with foil materials, the part played by specific factors in rubber to fabric adhesion is shown to be relatively unimportant. Specific factors do exist, and their magnitude is connected with the existence of polar groups or groups that can be polarized. The adhesion secured by the use of spun staple fiber effectively outweighs all other factors.

ACKNOWLEDGMENTS

The authors acknowledge with thanks discussion at the commencement of this work and some valuable criticisms during its progress from J. W. W. Dyer of the Ministry of Supply, Cardington, and B. C. Preece, then of the Ministry of Supply, Cardington, but not at the British Boot, Shoe, and Allied Trades Research Association.

REFERENCES

[1] Hammond and Moakes, *Trans. Inst. Rubber Ind.* **25**, 172 (1949).
[2] This issue of RUBBER CHEMISTRY AND TECHNOLOGY.

## III. EXAMINATION OF TEST TECHNIQUE

E. M. BORROFF AND W. C. WAKE

*Influence of rate of stripping on load required.*—In earlier work[1] a limited range of stripping rates was investigated, and the expected tendency was observed for unvulcanized cements to fail cohesively at low rates of stripping and adhesively at high rates. This is expected, because at low rates the deformation is viscous so that the load increases with the rate. With higher rates, appreciable flow of rubber no longer has time to occur, while the fraction of the highly elastic part of the deformation possible in the time becomes increasingly small, and fracture in the rubber becomes, with increasing rate of straining, more like brittle fracture. At some stage the stress required equals and then exceeds the strength of the adhesive bond, and failure occurs at the interface. Cohesive failures in unvulcanized cements are therefore expected at slow speeds and adhesive failures at higher speeds, the force recorded increasing with increasing speed and then approaching a limiting maximum which characterises the adhesion strength.

It has long been the practice in metal technology to assume that, in the failure of metals, the recorded strength varies proportionately with the square root of the rate of deformation. This has also been applied more recently to bitumens[2]. Accordingly, the data obtained in the experiments described below, were examined to see if such relationships could reasonably be applied. the equation:

$$\log (\text{stripping force}) = a + b \log (\text{rate of stripping in in. per sec.})$$

gives the required type of dependence of the stripping force on rate of stripping; and, in the case of the square root relation, $b = 0.5$. From the values obtained it would appear that $b$ can and does depart very much from 0.5, and it is doubtful if the occasions when this value is obtained are other than fortuitous.

The relationship specified by the equation must have a limited range, for it implies that a graph illustrating the dependence of force on rate would pass through the origin, and this is experimentally untrue. However, the equation could be corrected to allow for this, but for the present limited purpose, the much more involved computation is unnecessary. In fact, apart from estimating the values of the constant $b$ to ascertain if the suggested square root relationship held, it has been found not worth while to fit the constants to the data unless at least four different rates of stripping are available. For unvulcanized cements the most uniform data obtained were those from nylon fabrics reported in Part II[3], and these are presented in Table 1.

TABLE 1

STRIPPING FORCE IN POUNDS PER INCH WIDTH FOR NYLON FABRICS UNVULCANIZED CEMENTS

| | Natural rubber | | Polychloroprene | | Butadiene-acrylonitrile copolymer (Hycar OR-25) | |
|---|---|---|---|---|---|---|
| Rate of stripping | On heavy fabric | On light fabric | On heavy fabric | On light fabric | On heavy fabric | On light fabric |
| 2 in. per min. | 2.9 | 2.6 | 8.1 | 5.9 | 10.8 | 10.3 |
| 40 in. per min. | 9.0 | 7.5 | 9.7 | 7.0 | 26.4 | 16.1 |
| 66 in. per min. | 7.9 | 6.6 | 12.5 | 8.6 | 24.9 | 27.1 |
| 128 in. per min. | 7.3 | 4.4 | 11.5 | 8.4 | 27.3 | 17.8 |

The constant $a$ of the equation is the value of the log of the force required to strip at unit rate as estimated from the actual rates employed. Since its calculation involves the value of $b$ which has been discussed above, it is convenient to express the rates in inches per second so that unit rate falls somewhere near the mean of the rates actually used and thus avoids the extrapolation which would be necessary if the unit rate were to be measured in inches per minute. The value of $a$, therefore, is the best single parameter to use to characterize the strength of adhesion.

TABLE 2

CONSTANTS FOR REGRESSION LINE ILLUSTRATING ADHESION OF RUBBERS TO NYLON

| | Heavy fabric | | Light fabric | |
|---|---|---|---|---|
| Rubber | $a$ | $b$ | $a$ | $b$ |
| Natural rubber | 0.87 | 0.26 | 0.75 | 0.19 |
| Neoprene-GN | 1.04 | 0.09 | 0.90 | 0.09 |
| Hycar OR-25 | 1.40 | 0.24 | 1.28 | 0.17 |

The conclusions from the analysis of these results (from which the above figures are taken) are as follows:

Except for Neoprene, the differences between values of $b$ for different rubbers are not significant, and no differences in values of $b$ for the same rubber with light and heavy nylon fabrics are significant; $b$, it will be noted, is nearer to 0.25 than 0.5 for all cements.

For values of $a$, the standard deviation in original units is equivalent to 10 per cent of the strength, and about 28 per cent difference is required for significance. The stripping load at unit rate of stripping, for all cements is significantly greater for the heavy fabric than the light fabric.

It would be expected that purely mechanical factors would reflect a varying interaction of rate of stripping and type of rubber, as the modulus properties of rubber vary differently for different rubbers with rate of deformation. Further, the rate of deformation varies locally with the geometry of the weave, and differences between $b$ values for light and heavy nylons might be expected. This is not shown, in fact, and the low value of $b$ in the case of Neoprene does not fit in with the similarity of its modulus properties to those of Hycar-OR.

The considerations advanced regarding the dependence of the bond strength on the rate of stripping apply equally cogently to vulcanized cements. It would appear that when the rubber has been stiffened by vulcanization, rates of stripping of 40 to 66 inches per minute are sufficiently great for the maximum bond strength to have been realized, since there are on an average no significant differences between figures recorded at these rates for vulcanized cements. The bond strengths at a rate of stripping of 2 inches per minute are invariably lower. As, therefore, it appears that figures obtained at 40 and 66 inches per minute have attained the limiting maximum referred to earlier, it is figures at these rates that should be quoted as the bond strength.

*Variation of bond strength with period of vulcanization.*—It is convenient to represent the bond stripping force necessary as a resultant of two processes each having a characteristic force—period of vulcanization relation. The first is the gradual building up of cohesive strength as vulcanization proceeds.

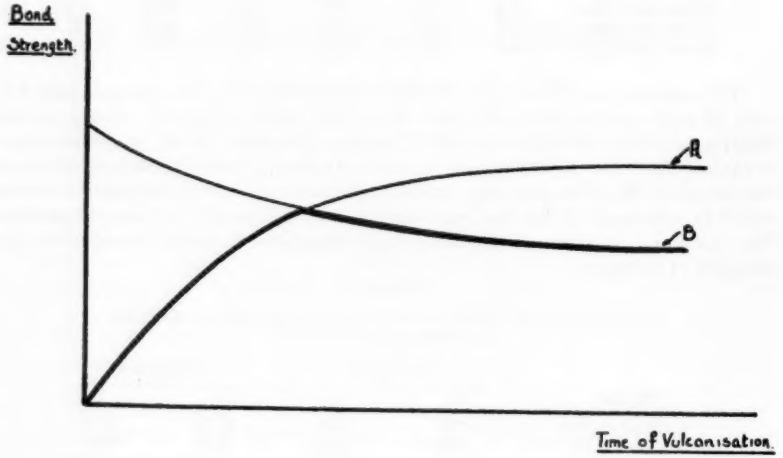


FIG. 1.

This we represent as curve A in Figure 1. The second is an apparent falling off of adhesive strength as vulcanization proceeds (curve B); the reason for this apparent falling off is discussed later. The resultant is shown by the heavy lines in Figure 1 and is seen to possess a maximum with cohesional failure of bond to the left of the maximum and adhesional failure to the right.

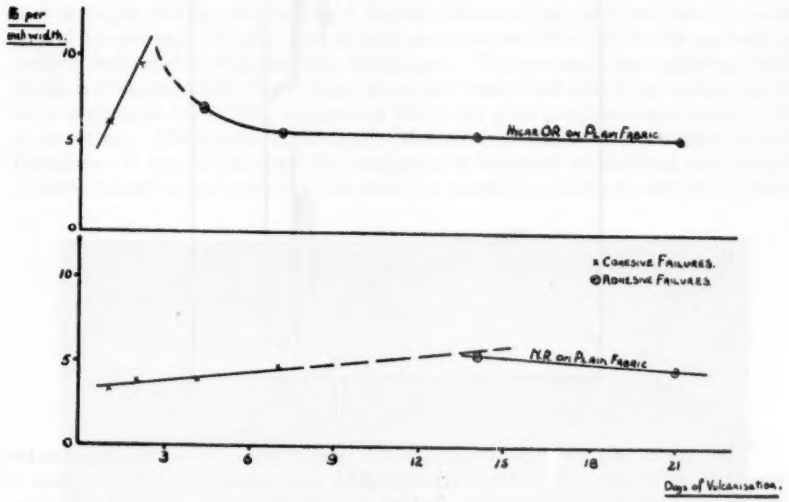


FIG. 2.

This is illustrated in Figure 2, where some of the results obtained for butadiene-acrylonitrile copolymers and natural rubber on a 7-oz. cotton duck are plotted. In all cases cohesional failures are found to the left and adhesional to the right of the maximum. In a few cases, as for example with continuous-filament nylon illustrated in Figure 3, where adhesional strength is low, the intersection of curves A and B of Figure 1 seems to have been passed before the time of the first cure. This would result from a general downward vertical displacement of curve B with respect to curve A; a smooth curve of bond strength gradually decreasing with time of cure, all values being fairly low, would then be expected, and is found.

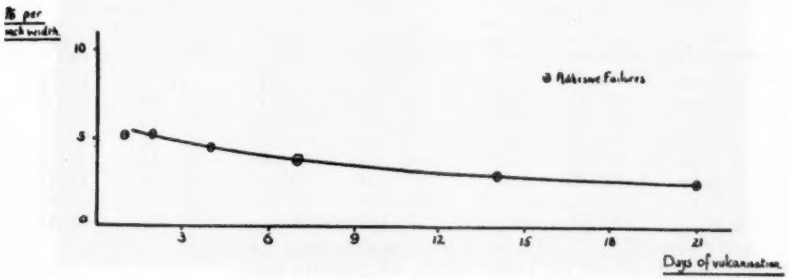


FIG. 3.

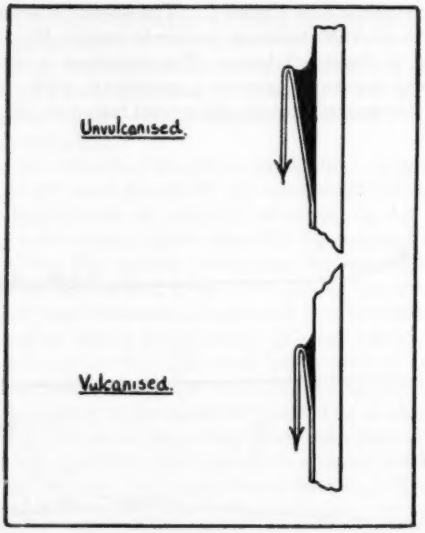


FIG. 4.

The general shape of the strength of the bond/period of vulcanization curve was thought to be due to the variation with vulcanization of the amount of rubber deformed, and therefore of the areas bearing the load. This is illustrated in Figure 4. In the unvulcanized material, flow can occur, and the load is distributed over a fair amount of interface. This is not possible with vulcanized rubber, and as it progressively stiffens in vulcanization the area of interface taking the load seems progressively to lessen; hence the apparent fall in bond strength with increasing degree of vulcanization. To test this point, a number of short wooden cylinders with right circular ends were made of close-grained hard wood to which a doubled ballonet fabric was cemented on the plane surface, the overhanging material being pleated back and wired into a

TABLE 3

DIRECT TENSION ON TEST: VARIATION OF FORCE (LB. PER SQ. IN.) WITH TIME OF VULCANIZATION

| Period of vulcanization | Smoked sheet | | Neoprene-GN | | Hycar OR-25 | |
|---|---|---|---|---|---|---|
| | Load for separation | Mean load | Load for separation | Mean load | Load for separation | Mean load |
| 7 hours | 10 | 10(C) | 10 | 10(C) | 10 | 10(C) |
| 16 hours | 40; 35 | 38(C) | 35; 48 | 42(C) | 42; 41 | 42(C) |
| 1 day | 61; 62 | 62(C) | 89; 83 | 86(C) | 65; 56 | 61(C) |
| 2 days | 62; 61 | 62(C) | 70; 95 | 83(M) | 65; 58 | 62(C) |
| 4 days | 65; 63 | 64(C) | 100; 82 | 91(M) | 59; 53 | 56(C) |
| 7 days | 62; 73 | 68(C) | 103; 82 | 93(A) | 72; 70 | 71(A) |
| 14 days | 93; 81 | 87(M) | 150; 130 | 140(A) | 110; 119 | 115(A) |
| 21 days | 106; 78 | 92(A) | 153; 163 | 158(A) | 122; 81 | 102(A) |

A: Adhesive failue, *i.e.*, failure at the adhesive-fabric interface.
C: Cohesive failure, *i.e.*, failure within the adhesive layer.
M: Mixture of A and C.

groove. These were cemented together in pairs with the vulcanizing cements, and it was found that the load required to separate increased linearly with period of vulcanization after the first day. This is clearly shown by Table 3.

It may be taken, therefore, that although the load required to strip falls with increasing vulcanization, the actual strength of the bond increases. It follows obviously that, if resistance to stripping is the criterion of adhesion, the highest test strength will be recorded by a cement which is only just sufficiently cross-linked to prevent cohesive failure and not so cross-linked that the amount of rubber deformed is reduced to a minimum. The picture here advanced supports and explains the observation in earlier work that adhesion appears to be at a maximum for lightly vulcanized films and gets progressively poorer with over curing. The question then arises as to the suitability of the stripping test. Certainly, it cannot be used for comparisons between vulcanized and unvulcanized cements, and even for comparisons between vulcanized cements results

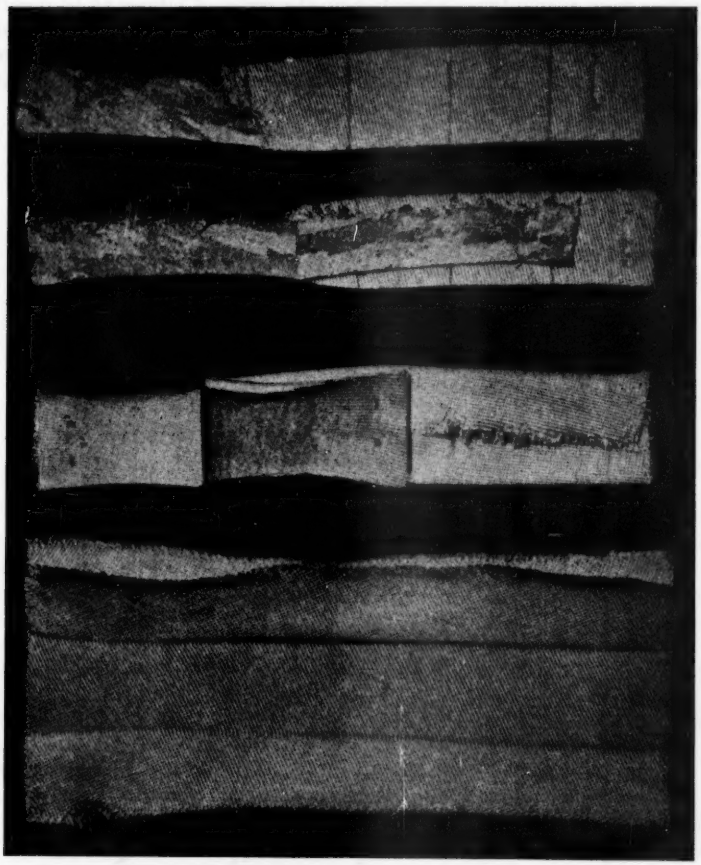

FIG. 5.

may reflect differences in moduli rather than strength of bond. The problem and its practical application is referred to again later.

*Improved stripping test.*—During the earlier stages of this investigation the stripping test used was that described by Moakes and Hammond[1] except that in place of 10 readings of load taken every ½-inch on three test-pieces it was realized that the work of testing could be reduced without serious loss of precision by the taking of readings at intervals of 1 inch only on two instead of three test-pieces. It was found by examination of typical results that differences between test-pieces were highly significant compared with the variation within test-pieces. The precision of the determination of the stripping load of any one test-piece by taking the mean of the ten readings was, therefore, wasted. The standard error of the mean of three test-pieces was 2.5 per cent of the load, or if only two pieces were used, 3 per cent. This latter figure seemed entirely adequate and two pieces only were used in all subsequent work.

The rest of the test procedure was satisfactory with 2-ply ballonet fabric but difficulties were encountered when testing the series of fabrics to be described in Part IV[4]. With these fabrics, fraying occurred at the edges of the test-piece, causing an increase in load and frequently the complete loss of the test-piece by tearing across from the point of initiation of fraying. To overcome this an alternative test-piece was devised for stripping tests.

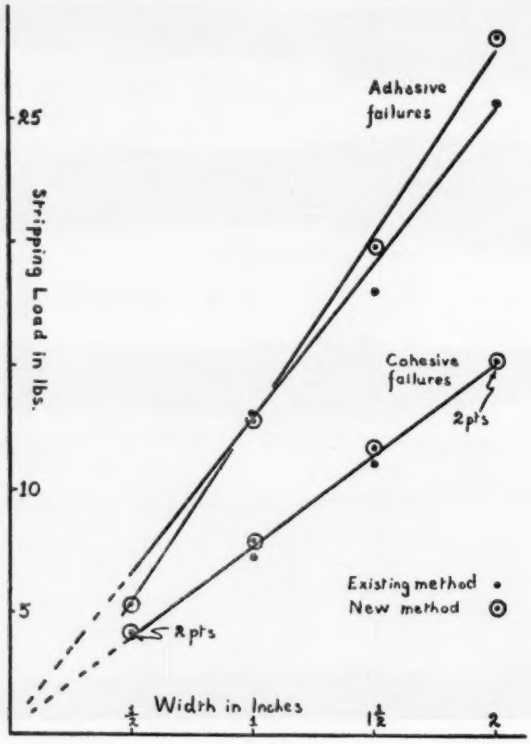


FIG. 6.

Pieces of fabric 3 × 16 inches were cut and a 1-inch width of both sides of the length of the strip were ironed underneath the central portion. Cement was applied to this middle strip only. After coating, the strips were folded in half, and dried or cured as necessary. The resulting test-piece consisted of a 1 inch wide cemented portion as in the old type of strip but with a 1-inch border of unproofed fabric on each side. This new method of preparing these test-pieces proved to be completely satisfactory, and no cases of fraying or failure of the fabric were met with. A photograph is shown as Figure 5.

To investigate edge effects, *i.e.*, departure from proportionality of load with width, a series of experiments were carried out using cotton duck and both old and new test-pieces 0.5, 1.0, 1.5, and 2.0 in. in width. Cohesive failures were obtained by using unvulcanized rubber and adhesive failures by using a self-vulcanizing compound. The results, illustrated in Figure 6, show that no true edge effect exists with cohesive failures, although some departure from a straight line is shown with the old type test-pieces. With adhesive failure an

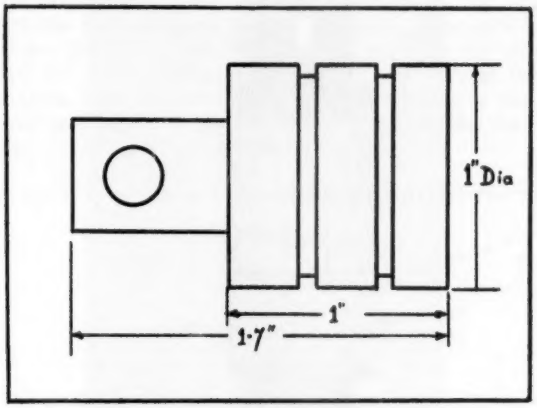


FIG. 7.

edge effect exists with the new test-pieces, as shown by the intercept on the axis when the best straight line is extropolated, but is not of much consequence. The older type test-piece shows some scatter about the straight line. The rate of stripping in these experiments was 40 inches per minute. In subsequent work with specially woven fabrics, the new stripping test was used with the folded test-piece.

*Direct tension test.*—In addition to the folded test-piece for stripping tests, the method already mentioned for measuring the adhesion by direct tension test was further developed and used. The technique already described was satisfactory with some fabrics, but with others the fabric left the wooden former before the bond being investigated was broken. In these cases one or two large-headed tacks were inserted to assist the adhesion of the fabric to the former. The full procedure was as follows. Pairs of close-grained hard wood cylinders (see Figure 7) were taken and circles of fabric about 3 inches in diameter were cemented to them with the same cement as was being investigated. The fabric was pleated back and wired into the grooves provided.

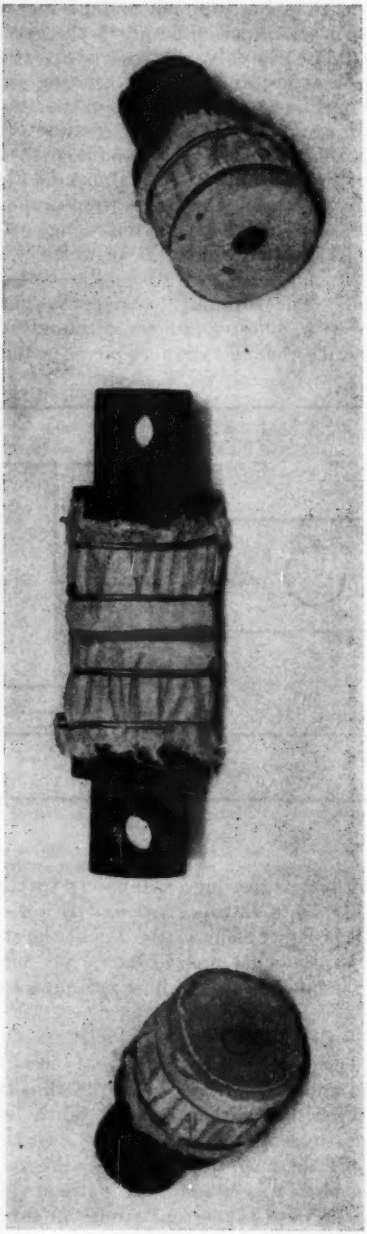

FIG. 8.

Usually one, but occasionally two, tacks were hammered home and cement applied with a spatula to the surfaces, which were combined after the cement film had almost dried out. The test was carried out by attaching with prepared grips to a Goodbrand cloth testing machine and the load recorded. The rate of separation of the grips of this machine was 4½ inches per minute. After fracture of the bond the rubber was stripped from the face to which it was still adhering, its thickness measured, and its exact area determined by tracing on to squared paper, the area of the tack-head being deducted. A photograph is shown of one test-piece made up and one broken (see Figure 8).

The differences between duplicate test-pieces (Table 3) show that when vulcanization had proceeded sufficiently for adhesive failures only to occur, a standard error of the mean of a pair of about 12 to 15 pounds was found. This figure is, apparently, independent of the actual value of the breaking load.

*Relation between stripping and tensile tests.*—It would be expected from the foregoing that the relation between the two types of test would be largely a function of the plasticity and modulus of the rubber and that some simple relationship should exist between the values obtained from the two tests over different fabrics but with the same cement. A good linear plot is obtained if stripping loads are plotted against direct tension loads for the series of fabrics reported in Part IV[3] with a natural rubber vulcanized cement (see Figure 9). With cements made from the other rubbers, the variations in the thickness of the cement layer used in the stripping tests tends to disguise the simplicity of the relationship.

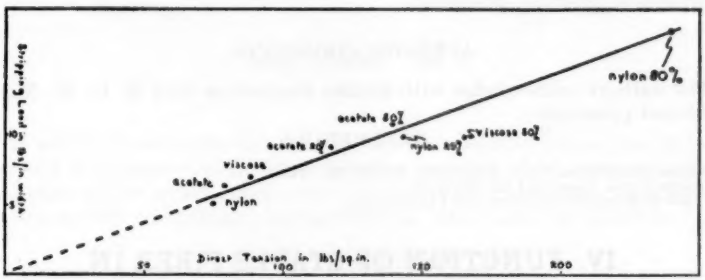


FIG. 9.

*Discussion of test procedure.*—An attempt to summarize may be made by indicating what information can be expected and is obtained from the testing of bonds when the failure is always an adhesion failure. With unvulcanized rubbers, the stripping test is very sensitive to rate of stripping, to thickness of rubber, and to temperature, because it measures the adhesion over an area which varies with the bulk properties of the rubber, which themselves vary with the rate of stripping. It is an adhesion test complicated by the rheology of the adhesive. With vulcanized rubber the stripping test becomes less sensitive to thickness, to rate of stripping, and to temperature, at the expense of sensitivity to the degree of cross-linking introduced by vulcanization. It measures the adhesion over a much smaller area than when testing unvulcanized cements, but this area is still defined by the property of the bulk rubber and not the interface. With vulcanized rubber, the direct tension test is preferable as a measure of adhesion, but it is scarcely to be recommended as a service or "proof"

test, since the test-piece has to be made specially. In garments or fabric-reinforced hose or conveyor belting, failure occurs in service by the stripping apart of two or more layers of fabric having a vulcanized interlayer between them. Such use is probably best simulated by the stripping test, and, in the case of belting, probably by stripping after fatigue by flexing. Used as such, the test should not be regarded as a measure of adhesion but as a measure of resistance to separation by stripping. Where failure is known to be due to shear or direct tensile pull, stripping will not give a useful indication of strength and may well grade bonds in an order different from the grading which would be obtained by shear or tensile test. The stripping test should not be used in comparative studies of cohesional or adhesional strengths of vulcanized and nonvulcanizing cements. It should be understood that by stripping, rates of at least 2 inches separation per minute are intended, and that the above remarks may not apply to very slow rate tests, which are more usually termed peeling tests.

SUMMARY

The variation with the rate of stripping of the load required to break rubber-to-fabric bonds is discussed for unvulcanized and vulcanized rubbers, and this is followed by a discussion of the load variation with period of vulcanization. The two features which are evident in stripping tests are separated, and a simple direct tension test is proposed as a more reliable measure of adhesion. An improved stripping test is proposed and this, together with the direct tension test, is discussed in a final section on the relation between the two tests and their application to practical problems.

ACKNOWLEDGMENTS

The authors acknowledge with thanks discussions with R. C. W. Moakes on the test procedure.

REFERENCES

[1] Hammond and Moakes, *Trans. Inst. Rubber Ind.* **25**, 72 (1949).
[2] Lethersich, *J. Soc. Chem. Ind.* **65**, 190 (1946).
[3] This issue of RUBBER CHEMISTRY AND TECHNOLOGY.

## IV. FUNCTION OF STAPLE FIBER IN RUBBER TO FABRIC ADHESION

E. M. BORROFF AND W. C. WAKE

The fourth part of this paper describes experiments with a series of fabrics specially woven to provide comparisons between spun staple fiber and continuous filament and between three chemically different filaments. These were the essential variables, and other features of manufacture were held as constant as possible. The materials chosen were viscose, acetate rayon, and nylon. The weave was a five-end satin weave, using either continuous filament or spun staple yarn as the weft. Owing to the nature of the weave used, one side of the cloth consists of 80 per cent weft, and the influence of the warp on adhesion is, therefore, small. It has already been indicated, and indeed is well known, that adhesion to spun staple yarn is much higher than to continuous flament yarn, and for this reason the side of the fabric containing 20 per cent staple was also used in the knowledge that a large part of the adhesion obtained was attribut-

able to the 20 per cent weft rather than the 80 per cent warp yarn on that face. Owing to the high cover factors (ends per in./$\sqrt{}$ count) in both warp and weft, the flattening of the threads combined with sideways spreading results in rather more than 80 per cent of the face surface and rather less than 20 per cent of the back surface being covered by weft. The percentages are, therefore, nominal rather than actual. Figure 1 illustrates the weave and shows the difference between the weft and warp faces. Both warp and weft were composed of 2-ply yarns and the twist was maintained as nearly as possible the same for all wefts. Since it is believed that this is the first reported instance of such a comparative study, the full specification of the fabrics used is reproduced as Table 1.

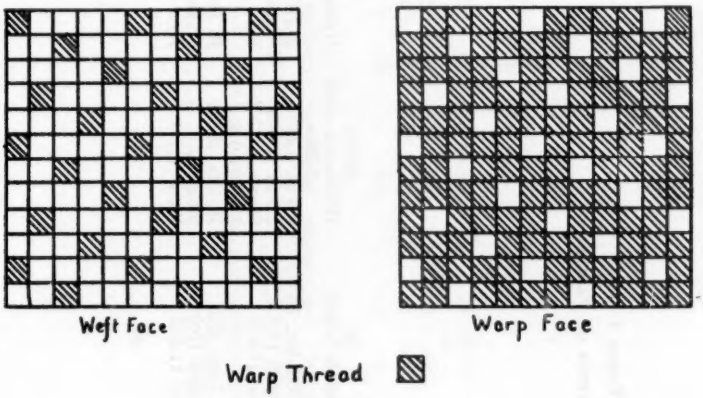


FIG. 1.

It will be shown later that, with the spun staple fiber fabrics, the individual fiber end is an important factor in adhesion in a way which was not realized at the outset of the investigation, and it is, therefore, unfortunate that the fibers are not strictly comparable, having differing mean radii calculated as follows:

| | |
|---|---|
| Viscose | 0.000599 cm. |
| Acetate | 0.000819 cm. |
| Nylon | 0.000965 cm. |

Stripping and direct tension tests were carried out with these fabrics, using the three self-curing cements described in the Part II[1], *viz.*, those based on natural rubber, Neoprene-GN, and Hycar OR-25. Preliminary experiments showed that an optimum cure for stripping test could be obtained by heating at 100° C in an oven for 10 minutes, and this was followed by conditioning at 25° C for 24 hours. Stripping was carried out at 40 inches per minute and the load recorded in pounds.

The stripping test is very sensitive to the thickness of the cement layer and, without great refinement of technique and apparatus, it is not possible to obtain identical thicknesses. Repetition is not satisfactory, since a different degree of vulcanization may interfere. It is usual, therefore, either to run a preliminary spreading or else to prepare several pieces with cement thicknesses differing by small amounts. Limitation of the fabric length prevented either of these alternatives, and this must be allowed for in any attempted interpretation of

TABLE 1

SPECIFICATION OF FABRICS

| Sample reference | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Warp yarn fiber | Viscose bright | | | | | |
| Warp yarn structure: | | | | | | |
| (1) Nominal | 2/150 den./27 fils.<br>Singles 10 tpi. S<br>Fold 10 tpi. Z | As<br>A | As<br>A | As<br>A | As<br>A | As<br>A |
| (2) Actual | R. den. 304<br>Singles 11 tpi. S<br>Fold 10 tpi. Z | | | | | |
| Warp sett (on table) end per inch | 67/68 | 68/69 | 68 | 68/69 | 68/69 | 70 |
| Weft yarn fiber | Viscose bright | *Fibro bright 2/26's | Acetate bright | †Fibroceta matt 2/26's | Nylon bright | Nylon matt 2/26's |
| Weft yarn structure | | | | | | |
| (1) Nominal | 2/200 den./36 fils.<br>Singles 15.5 S<br>Fold 11.0 Z | 1.5 fil. den.<br>$1\frac{7}{16}$ in. staple<br>Singles 15.5 Z<br>Fold 11.0 S | 2/200 den./38 fils.<br>Singles 15.5 S<br>Fold 11.0 Z | 2.5 fil. den.<br>2.5 in. staple<br>Singles 15.5 Z<br>Fold 11.0 S | 2/210 den./34 fils.<br>Singles 15.5 S<br>Fold 11.0 Z | 3.0 fil. den.<br>1.5 in. staple<br>Singles 15.5 Z<br>Fold 11.0 S |
| (2) Actual | R. Den. 410<br>Singles 15.4 S<br>Fold 11.8 Z | R. Cts. 13.2's<br>Singles Z<br>Fold 10.8 S | R. Den. 425<br>Singles 16.0 S<br>Fold 11.2 Z | R. Cts. 13.1's<br>Singles Z<br>Fold 11.3 S | R. Den. 470<br>Single 15.2 S<br>Fold 13.0 Z | R. Cts. 12.8's<br>Singles Z<br>Fold 10.8 S |
| Weft sett (on table) picks per inch | 65 | 65 | 66 | 65 | 66 | 65 |

* Trade name for Courtauld's production of viscose rayon staple.
† Trade name for Courtauld's production of acetate rayon staple.

TABLE 2

STRIPPING FORCE IN POUNDS PER INCH WIDTH FOR RUBBER CEMENTS ON CONTINUOUS FILAMENT AND SPUN STAPLE FABRICS

| | Viscose | | | | Acetate | | | | | | Nylon | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cont. fils. | | Weft face 80% staple | | Cont. fils. | | Warp face 20% staple | | Weft face 80% staple | | Cont. fils. | | Warp face 20% staple | | Weft face 80% staple | |
| | Thickness cement (in. × $10^4$) | Load (lb.) | TH | L | TH | L | TH | L | TH | L | TH | L | TH | L | TH | L |
| Smoked sheet | 22 | 7.0 | 26 | 9.9 | 49 | 6.4 | 52 | 9.2 | 57 | 10.8 | 66 | 5.1 | 68 | 9.9 | 54 | 17.4 |
| Polychloroprene | 73 | 14.1 | 76 | 22.4 | 29 | 8.6 | 32 | 12.3 | 42 | 15.6 | 53 | 8.1 | 40 | 15.6 | 40 | 21.1 |
| Butadiene-acrylonitrile copolymer (Hycar OR-25) | 61 | 15.4 | 76 | 22.4 | 48 | 14.1 | 45 | 15.4 | 40 | 17.0 | 40 | 9.0 | 44 | 15.4 | 55 | 18.3 |

Table 2. The load required to strip increases with increasing thickness of the cement layer due to spreading of the load over a larger area of interface. Adhesive failure was obtained in all cases.

The direct tension test-pieces were vulcanized by heating at 100° C for 1 hour, the longer time being required presumably either because of the difficulty in removing solvent from the cement or because of the large heat capacity of the wooden formers. Conditioning was carried out at 25° C for 24 hours. The test-pieces were then tested at $4\frac{1}{2}$ inches per minute, the loads were recorded in pounds. Adhesive failure was obtained in all cases.

With the staple fiber fabrics, both sides were used in different tests to investigate the effect of the amount of spun fiber staple on the adhesive strength.

The direct tension test is less sensitive to thickness than the stripping test. The results recorded in Table 3 refer to test-pieces with an average thickness of $241 \times 10^{-4}$ in. with a coefficient of variation of $\pm 20$ per cent. The figures marked with an asterisk were for test-pieces somewhat thinner than the rest and refer to test-pieces rather less than $50 \times 10^{-4}$ inch. It is not thought that this drop in thickness appreciably alters the test results.

TABLE 3

RESULTS OF DIRECT TENSION TESTS USING CONTINUOUS FILAMENT AND SPUN STAPLE FABRICS

Loads in lb. per sq. in.

| | Viscose | | | Acetate rayon | | | Nylon | | |
|---|---|---|---|---|---|---|---|---|---|
| Cement/Fabric | Cont. fil. | 20% staple | 80% staple | Cont. fil. | 20% staple | 80% staple | Cont. fil. | 20% staple | 80% staple |
| Natural rubber | 88 | 130 | 165 | 79 | 117 | 139 | 75 | 143 | 240 |
| Polychloroprene | 121 | 136 | 154* | 106 | 121 | 145 | 103 | 169 | 251 |
| Butadiene-acrylonitrile copolymer | 77 | 134 | 154* | 90 | 121 | 139 | 62 | 130 | 192 |

The results are conveniently summarized in Figure 2, where it can be seen that direct adhesion to continuous filament differs widely from rubber to rubber and that these differences largely disappear with the increased adhesion observed when staple fiber is incorporated in the fabric. With adhesion to continuous filament the differences observed must reflect the differing polarities of the rubbers, and possibly, but to a lesser extent, their differing mechanical properties. Even with 20 per cent staple fiber these differences are smoothed out almost completely for viscose and acetate rayon, and only persist as a smaller percentage effect in the case of nylon. The staple fiber becomes the determining factor for adhesion.

Bond failure with staple fiber is characterized by fracture of a number of the projecting fiber ends, and experiments were made to count the number projecting from unit area, to determine the number and size distribution of these fractured, and to determine the breaking strength of the individual staple fiber.

*Properties of the staple fiber.*—The numbers of the fiber ends projecting from the surface were determined by mounting a folded piece of the fabric between two microscope slides, placing on the micrometer stage of a microscope, and projecting the image on to a ground glass screen. The fiber ends recovered from the fractured bond were determined for natural rubber by swelling the rubber to allow removal from the cloth to which it was still adhering without

damage to the fiber ends of that piece of cloth, and then heating the piece of vulcanized rubber in *p*-dichlorobenzene under conditions of free access of air so that it dissolved. The solution was diluted and filtered, and the fiber fragments were dried and weighed. A reasonable proportion of these pieces were taken, usually between 300 and 400, and were counted and weighed. Samples of 100 were then placed on a microscope slide, and the length of each fragment was measured with a micrometer eyepiece. From these measurements the length distributions shown were obtained. The numbers of project-

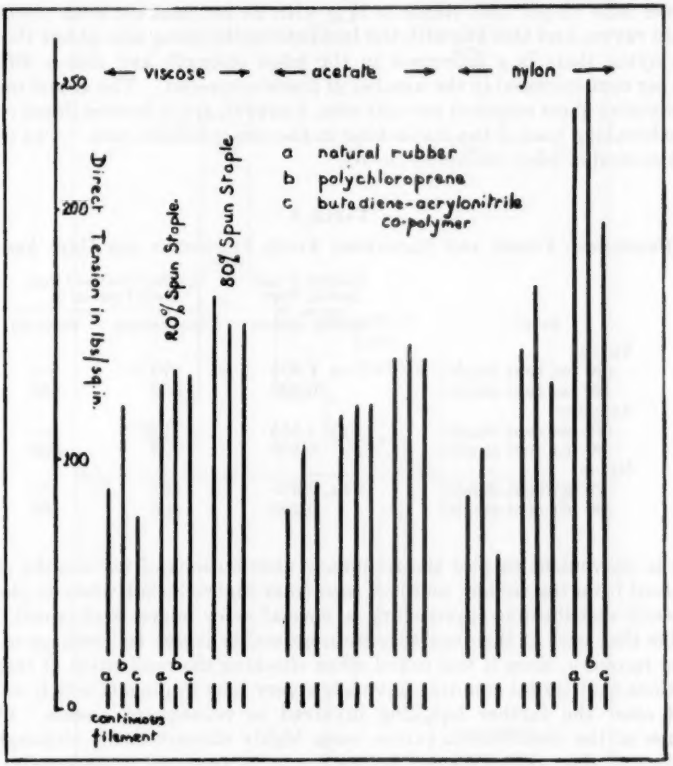


FIG. 2.

ing fiber ends were estimated only for the weft face of the fabric; the figures for the warp face (20 per cent staple) given are based on the estimate of the weft face. Table 4 shows the number of projecting fibers present initially, the number of fiber ends recovered per square inch from the cement for the direct tension test and some of the data for the stripping test for natural rubber cements only.

The breaking strengths of the staple fibers were obtained by examination of the staples untwisted from the yarn. These were tested with a light calibrated spring, the extension of which was measured against graph paper, the specimen

being fastened to grips by sealing-wax and the extension applied manually at as uniform a rate as possible to the end remote from the spring. A number of fibers of each type were tested; the mean breaking loads together with the standard error of the mean calculated from the dispersion of the results were:

Viscose 4.7 gram wt. ± 0.10 equivalent to a tenacity of 3.1 g. per denier.
Acetate 3.0 gram wt. ± 0.26 equivalent to a tenacity of 1.2 g. per denier.
Nylon 15.0 gram wt. ± 0.18 equivalent to a tenacity of 5.0 g. per denier.

The number of fibers fractured when the bond breaks is much the same for the face with 80 per cent staple as it is with 20 per cent for both viscose and acetate rayon, and this fits with the bond strengths being also about the same. With nylon there is a difference in the bond strength and also a difference (12.5 per cent increase) in the number of fibers recovered. The actual numbers of projecting fibers removed per unit area, however, are in inverse linear relation to the breaking load of the staple fiber in the direct tension test. The relation is not so simple when stripping occurs.

TABLE 4

PROJECTING FIBERS AND RECOVERED FIBER FRAGMENTS PER UNIT AREA

| Fabric | Number of projecting fibers per sq. in. Initially present | Number recovered from cement per sq. in. | |
|---|---|---|---|
| | | Direct tension | Stripping |
| Viscose: | | | |
| (20 per cent staple) | *ca.* 1,605 | 619 | — |
| (80 per cent staple) | 6,420 | 652 | 465 |
| Acetate: | | | |
| (20 per cent staple) | *ca.* 1,615 | 762 | — |
| (80 per cent staple) | 6,350 | 723 | 833 |
| Nylon: | | | |
| (20 per cent staple) | *ca.* 2,315 | 361 | — |
| (80 per cent staple) | 9,260 | 406 | 161 |

It is convenient to plot the frequency distributions of log lengths of fiber recovered from the rubber, and it is seen from Figure 3 that when so plotted a frequency distribution approaching a normal error curve is obtained. It is possible that part of the departure from normality is due to breakage of fibers during recovery, since it was found when checking the replication of these distributions that initial counting gave a few very long fragments which were not found after the further handling involved in subsequent counts. Certain features of the distribution curves seem highly characteristic, although confirmation of this will be needed before it can be accepted unreservedly. The length distribution of fibers recovered after fracture of a bond to viscose shows no fragments longer than antilog 2.6 and none shorter than antilog 1.2. (The length units correspond to the arbitrary divisions of the micrometer eyepiece of the microscope used and 1 unit = .0016 cm.) If it is assumed that, with spreading from solution, all fibers which project from the fabric surface are embedded in the rubber, then most of all lengths pull out without fracture and all the shorter fibers do so. After bonding to acetate rayon, fiber fragments in the log range 1.1 to 1.2 are recovered, suggesting that either this is due to the known weaker strength of the acetate staple (breaking load of 3.0 grams compared with 4.7 grams for viscose) or to the rubber holding the fibers more firmly, or of course, to a combination of these factors. As, however, adhesion

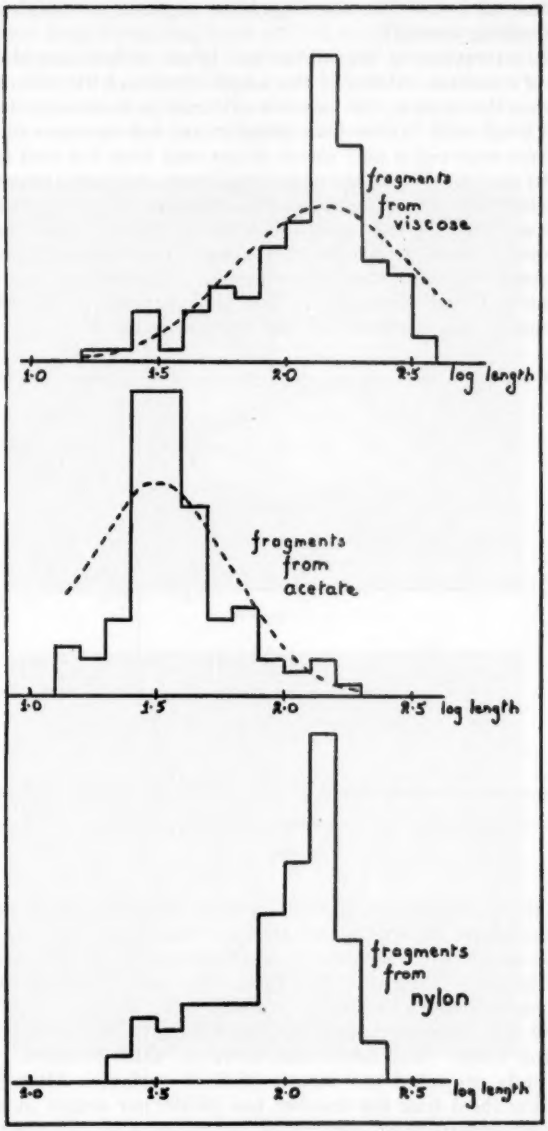


FIG. 3.

to continuous filament fabrics does not differ much, the former is the most probable explanation. The shortest nylon fibers recovered from the rubber cement lie in the log range 1.3 to 1.4, and this is almost certainly a reflection of the much higher breaking load of the nylon material. Greater area of fiber

must be embedded before the shearing force required to withdraw the fiber exceeds its breaking strength.

If the sole interaction of the rubber and fabric on breaking the bond were the fracture of a certain number of the longer fibers and the withdrawal of the remainder from the cement, the fabric would not be materially different after breaking the bond with rubber from what it was before, since the number of projecting fibers removed is only about 10 per cent from the weft face containing 80 per cent staple. Where the projecting fibers are fewer a larger proportion of them is removed. Experiment showed, however, that the fabric was considerably changed by the mechanism of bond fracture. A self-curing natural rubber cement was spread on to the weft face of the acetate rayon fabric and, when vulcanized, was separated by stripping. This process was repeated on the same piece of fabric three times. The load required to strip the first time was 10.6 pounds, the thickness of the cement being $44 \times 10^{-4}$ inch. The

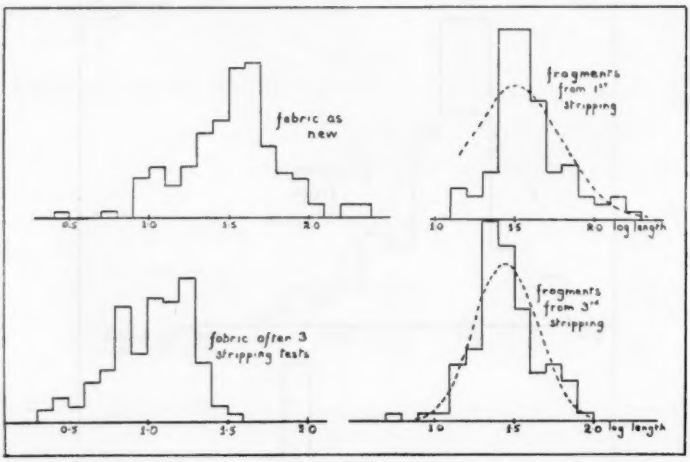


FIG. 4.

second time the load required fell to 9.7 pounds, but the drop observed may be completely accounted for by the fact that the cement was only $37 \times 10^{-4}$ inch thick on this occasion. The third time of stripping required a load of 11.0 pounds, the thickness being $45 \times 10^{-4}$ inch. The stripping load was, therefore, apparently unaffected by the previous history of the fabric. After the first stripping, 833 fiber fragments were recovered for each square inch of area, and after the third, 1,058. The fabric was, however, much changed. When new, 6,350 fiber ends projected per square inch of surface. After it had been stripped for the third time the number was 23,900 per square inch. Figure 4 gives the length-distribution histograms for samples of 100 plotted on a log scale. No fibers of log length greater than 1.8 exist on the fabric after its third use, even though the number of fibers projecting has more than trebled. The peak of the distribution is widened very considerably, and the mean has shifted from 1.45 to 1.21, although the mode has only shifted from 1.55 to 1.45. Figure 5 shows a microphotograph of a profile of the fabric and illustrates

that the appearance of the fabric is changed from a glossy surface, that is hairy with moderately long straggling hairs (*a*), to a dull furry surface (*b*). The length distributions of fiber ends recovered from the rubber (also shown in Figure 4) from the initial and the third cement layer are much more similar than those of the fiber projecting from the fabric. Their modes are not very dissimilar, and their means are only slightly different (1.94 and 1.40). During

FIG. 5*a*.

FIG. 5*b*.

breaking of the third bond, quite short fragments are left in the cement and, as is to be expected, no very long ones are to be found, as they have been previously stripped off.

The picture thus presented of the breaking of a rubber-to-fabric bond is by no means entirely simple, but there is little doubt that by far the most important factor in determining the strength of bond is the breaking strength of the

individual fiber. The number that are broken is only a small fraction of the total when this total is large, and the proportion broken seems to increase with decreasing total fibers projecting. It follows, therefore, that it is not essential to have a fabric composed entirely of spun staple yarn to obtain good adhesion.

*Requirements for good rubber-to-fabric adhesion.*—The picture that emerges from bringing together the factors so far investigated is sufficient to enable the requirements for good adhesion to be stated for simple systems. By simple systems we mean rubber cements as ordinarily compounded, spread on untreated fabrics. No evidence has been presented which would justify the extension of our conclusions to adhesion to fabrics which have been treated with casein and rubber latex mixtures of the more recently introduced treatments involving resorcinol-formaldehyde resins or isocyanates.

Efficient adhesion involves mechanical rather than specific factors, and the mechanical factors which are important are a question of the yarn structure rather than the fabric structure or weave. An open fabric to secure good penetration of the rubber would seem, from the evidence advanced in Part I[1], to be important only where it is desired to secure continuity of the rubber from one side of a fabric to the other. This would be important, for example, in a multiple power transmission belt, but the continuity of the rubber structure thus obtained does not necessarily increase the adhesion of the rubber to the fabric. It is essential for good adhesion that the ends of the staple fiber should penetrate into the rubber and not that the rubber should penetrate into the weave of the fabric.

As it has been shown that the strength of the bond is related to the strength of the staple fibers and that in any bond failure the fraction of these that are broken varies with the number available, it follows that it is not necessary to use a fabric woven or knitted entirely of spun staple yarn. There are, indeed, many reasons why this should not be done. For many purposes it is convenient to form the warp entirely of continuous filaments, and thus obtain the maximum strength and minimum stretch. The weft can then be of a mixture of a spun staple fiber yarn and continuous filament[2]. Little loss of weft strength would result from using 1 pick in 4 of spun staple and forming the remaining 3 of continuous filament. If the spun staple was of nylon such a structure would have adhesion to rubber of the same order as an all-cotton fabric. The essence of the structure is to insert in the weft sufficient spun staple yarn to achieve the required degree of adhesion; the smaller the amount of staple to be inserted, the greater the need to use material of high breaking strength.

The production of proofed fabrics with a high degree of sheen on the fabric could be assisted by the use of a satin weave and only a portion of the weft to contain spun staple yarn. The cloth would be proofed on the weft face, leaving the fabric side of the proofing with only a minimum of spun staple in it, something of the order of 5 per cent.

Even at this early stage of the investigation, therefore, it does seem that some practical suggestions emerge and should be tried.

## SUMMARY

An investigation of the adhesion of rubbers to a series of fabrics woven from spun staple and continuous filament viscose, acetate rayon, and nylon is described. Using the direct tension test, it is shown that adhesion strength is a property of the staple fiber and is directly related to its tensile strength. The number of projecting fibers has been determined and compared with the broken-

off ends recovered from a natural rubber cement after stripping from the fabric. The size-distribution histograms of the recovered fiber ends are also given and discussed. Recommendations are made for utilizing the results so far obtained in this investigation for the production of improved rubber-textile articles.

## ACKNOWLEDGMENTS

It is a pleasant duty to record the help which we have received from W. E. Morton and J. M. Preston of the College of Technology, Manchester. In addition to discussions, Professor Morton designed and arranged for the weaving of the special fabrics at the College of Technology. The yarns were supplied by the courtesy of Messrs. Courtaulds Ltd., and our thanks are due to H. Ashton of Arrow Mill, Rochdale, who was responsible for the yarn structure and through whom the yarns were obtained. We must also record our thanks to various of our colleagues and to G. L. Hammond of the Ministry of Supply, with whom we have discussed adhesion and, lastly, to the Research Association of British Rubber Manufacturers and the Ministry of Supply, MX4b (Advisory Service on Rubber and Plastics) for permission to publish this interim account of a joint program of research on adhesion.

## REFERENCES

[1] This issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[2] Application has been made for patent protection to cover specific textile constructions and uses arising from this.

# STAINING PROBLEMS ASSOCIATED WITH RUBBER CHEMICALS *

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*Introduction.*—This paper describes a program of systematic work carried out on staining phenomena associated with vulcanized rubber. It is realized that information on the subject must inevitably exist within the industry, but it is thought that it consists largely of isolated facts. An attempt has, therefore, been made to gather together the parts so as to present the picture as a whole and at the same time to explore various practical applications where staining is of paramount importance.

*Definitions.*—First of all, it is important to define what is meant by "staining" for in the past the word has been used loosely,, and only too often have rubber chemicals been described vaguely as staining or nonstaining, without any further qualification. It should be recognized that not only are there degrees of staining but also different types of staining. Thus, it is not always safe to imagine that the use of a staining type of antioxidant in a black mix is of no consequence, as it can cause staining of some other material which may be in contact with the rubber in service. Also, an antioxidant normally regarded as belonging to the nonstaining class can give rise to serious discoloration by reaction with some other ingredient of the mix.

In the course of this work, a definite distinction has been made between "coloration", "discoloration", and "staining by migration".

*Coloration* is defined as the color of the vulcanizate immediately after cure.

*Discoloration* as the change in color which occurs on the surface of the rubber article when it is exposed to light.

*Staining by migration* refers to the staining which becomes evident on the surface of some material, not necessarily rubbery in constitution, which has been in contact with a rubber article containing a staining ingredient.

Finally, there is finger marking. This refers to the facility with which certain compounds show finger marks immediately after cure.

It should be noted that these definitions may differ materially from definitions given in the past, and it is emphasized that, when talking of staining, the meaning of the terms used should be clearly understood. The above definitions, however, are substantially in line with those given in recent American and Canadian publications[1], except that in the latter the word *pigmentation* is used for *coloration*, while *staining* is employed instead of *staining by migration*. The authors prefer the last named term as more specific and to retain the word *staining* to describe the phenomenon as a whole, as, for example, in the term *nonstaining antioxidant*. The two systems are given in Table 1.

*Ultraviolet lamp and ordinary daylight.*—Staining is a visual phenomenon, and the only test apparatus employed in the experimental work has been the ultraviolet lamp for accelerating the discoloration effect.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 4, pages 265–286, December 1949.

The ultraviolet lamp consists of a 240-volt, 370-watt mercury discharge bulb, suitably hooded to project its light downwards and placed at a height of 12 inches above a table of 15 inches diameter, which rotates at 1 revolution per minute. For routine tests, the test-specimens employed are the $1\frac{3}{4}$ inch diameter center discs from Schopper tensile test-rings. These are placed around the perimeter of the revolving table, only a portion of the disc being exposed to the lamp at one time so that any change in color may be readily observed. If the test-specimens are too large and project too near the center of the table, a definite difference in the degree of discoloration over the surface of the specimen is observed, due to the difference in intensity of the incident light.

It is the authors' experience that all vulcanized rubber discolors to a light yellow color after a few hours under the U.V. lamp, the degree of discoloration depending on the various ingredients of the mix.

It is recognized that this yellowing effect appears to be accelerated abnormally by exposure to U.V. light. For example, if a rubber compound containing a staining antioxidant is exposed to ordinary daylight, the discoloration due to the antioxidant develops long before any yellowing of the compound takes place, and the true color of the antioxidant discoloration is clearly visible. On exposure to U.V. light, however, the antioxidant discoloration and the yellowing tend to develop simultaneously and the resultant effect is additive.

TABLE 1

TERMS USED TO DESCRIBE STAINING PHENOMENA

| Description | Proposed term | American term |
|---|---|---|
| Color imparted to unexposed cured compound | Coloration | Pigmentation |
| Color developed by exposure to light | Discoloration | Discoloration |
| Staining imparted to adjacent material | Staining by migration | Staining |
| Facility of compound to show finger marks | Finger marking | |

To illustrate this, a compound was taken containing a good nonstaining accelerator, tetramethylthiuram monosulfide. On exposure to the U.V. lamp, it developed a pale yellow color, whereas in daylight no discoloration was evident, after several weeks' exposure. The second compound was as the first, but contained *sym.* di-$\beta$-naphthyl-*p*-phenylenediamine as antioxidant. In daylight this antioxidant caused a characteristic gray discoloration, but under the U.V. lamp this was so masked by the development of the yellow discoloration that the resultant effect could only be described as a dirty yellow.

Further, as the yellow color becomes more intense with prolonged exposure under the U.V. lamp, one may get the impression that compounds tend to level up to the same degree of discoloration with the passage of time, whereas tests in ordinary daylight show this is not the case.

Another point is that when rubber samples are exposed to daylight, there is first a bleaching action. This is true also for U.V. light, but it does not persist for long before yellowing commences. The effect is obviously more noticeable with compounds that suffer from a certain amount of coloration before exposure, for example, with vulcanizates containing guanidine or aldehydeamine accelerators. On the other hand, if titanium dioxide is included in the mix, the coloration is masked, and the bleaching effect may not be observed.

A similar bleaching effect on exposure to daylight has been observed[2] with Neoprene.

So long as the limitations of the U.V. lamp are realized, it can be used successfully in the speedy assessment of the tendency of compounds to discolor on exposure to light. After all, the main use of the U.V. lamp is not to examine the characteristics of rubber chemicals which are known to discolor, but to distinguish fine differences between those that are said not to discolor. Thus, in the evaluation of nonstaining antioxidants, the U.V. lamp provides the only way in which speedy and accurate results can be obtained.

Finally, with reference to the difficult question of what are the relative times of exposure to the U.V. lamp and to daylight to give comparable discoloration, it will be readily appreciated that many factors, such as the different conditions possible in setting up the U.V. test, the variation of daylight, the fact that the type of discoloration is different under the two sources of light, and that some forms of discoloration develop relatively more quickly under one source than the other, all make an exact correlation impossible. As a rough guide, it has been found that 24 hours under the U.V. lamp employed in this investigation was equivalent to 6 months' daylight exposure.

An apparatus has been described[3], based on the U.V. lamp, which is said to give positive results as to whether a compound will discolor or not in 30 minutes. Although this may certainly be adequate as a rough guide, it is the authors' opinion that where the best nondiscoloring compounds are being developed and where fine differences in discoloration are important, longer periods of exposure are necessary. With the apparatus described above, exposure tests are normally carried out for periods of 6 to 48 hours.

*Effect of the rubber.*—In considering the factors which cause coloration and discoloration, it is necessary first to look at the rubber itself.

Table 2 shows the color of various natural and synthetic rubbers in the raw state and of examples of their vulcanizates, both with and without the addition of titanium dioxide. On the bottom line the effect of exposing the vulcanizates to the U.V. lamp is indicated.

For the whitest compounds or where the brightest colors are desired, pale crepe is preferable to smoked sheet. The coloration due to the darker color of the smoked sheet is quite definite and, though it can be largely offset by the addition of titanium dioxide, it still persists to a small extent even when an addition of 10 per cent of titanium dioxide (on the rubber content of the mix) has been made.

With some synthetic rubbers, the raw polymer is such that it is impossible to obtain a white compound unless relatively large amounts of titanium dioxide are incorporated. This is particularly true for GR-S, Neoprene-GN and Vulcaprene. Perbunan and Hycar OR-15 give vulcanizates of roughly the same color as those obtained with smoked sheet. Excellent whites can be obtained with Butyl. Furthermore, some of the synthetic products also discolor heavily on exposure to light, notably GR-S, Neoprene-GN and to a lesser extent, Butyl. Vulcaprene is remarkably free from discoloration on exposure to light.

With GR-S, the discoloration is to be expected, as it contains phenyl-$\beta$-naphthylamine, which is well known as a staining antioxidant. American synthetic rubber manufacturers are now fully alive to the disadvantage of marketing a product which discolors on exposure to light, and new polymers, such as GR-S 25, described as nondiscoloring, are being introduced to the trade.

At this point, it would be pertinent to describe the natural-rubber compound used in this work to evaluate the staining properties of rubber chemicals. The

TABLE 2

EFFECT OF THE TYPE OF RUBBER ON COLORATION AND DISCOLORATION

| | Pale crepe | Smoked sheet | GR-S | Perbunan |
|---|---|---|---|---|
| Color of raw material | Pale yellow, darker when milled | Brown, paler when milled | Black, very dark brown when milled | Amber |
| Mix used | Pale crepe 100<br>Zinc oxide 10<br>Blanc fixe 75<br>Stearic acid 1<br>Sulfur 2.5<br>Vulcafor-MS 0.5 | Smoked sheet 100<br>Zinc oxide 10<br>Blanc fixe 75<br>Stearic acid 1<br>Sulfur 2.5<br>Vulcafor-MS 0.5 | GR-S 100<br>Coumarone resin 15<br>Zinc oxide 10<br>Blanc fixe 86<br>Stearic acid 1<br>Sulfur 0.8<br>Vulcafor-MS | Perbunan 100<br>Coumarone resin 15<br>Zinc oxide 10<br>Blanc fixe 79<br>Sulfur 0.5<br>Vulcafor-MS 2 |
| Cure at 141° C | 10 min. | 10 min. | 30 min. | 50 min. |
| Amount of titanium dioxide added (based on rubber content) | 10 per cent | 10 per cent | 20 per cent | 20 per cent |
| Color of compound (without titanium dioxide) | Off white | Light brown | Brown | Equal to smoked sheet |
| Color of compound (with titanium dioxide) | White | Slightly darker than pale crepe | Pale brown | Equal to smoked sheet |
| Discoloration on exposure to U.V. lamp (48 hrs.) | Pale yellow | Slightly darker than pale crepe | Very dark brown | Equal to smoked sheet |
| | Hycar OR-15 | Butyl | Neoprene-GN | Vulcaprene-A |
| Color of raw material | Fawn | Transparent, whitish when milled | Pale brown, darker when milled | Fawn |
| Mix used | Hycar OR-15 100<br>Coumarone resin 15<br>Zinc oxide 10<br>Blanc fixe 79<br>Sulfur 0.5<br>Vulcafor-MS 2 | Butyl 100<br>Zinc oxide 10<br>Blanc fixe 75<br>Sulfur 2.5<br>Vulcafor-TMT 1.0<br>Vulcafor-ZDC 1.5 | Neoprene-GN 100<br>Magnesium oxide 4<br>Zinc oxide 5<br>Blanc fixe 56<br>Dibutyl phthalate 3 | Vulcaprene-A 100<br>Blanc fixe 40<br>Stearic acid 1<br>Vulcafor-VHM 7.5<br>Vulcafor-VDC 0.75 |
| Cure at 141° C | 50 min. | 45 min. | 60 min. | 35 min. plus 2 hrs. at 125° C |
| Amount of titanium dioxide added (based on rubber content) | 20 per cent | 15 per cent | 11 per cent | 15 per cent |
| Color of compound (without titanium dioxide) | Equal to smoked sheet | Whiter than pale crepe | Very dark brown | Dark brown |
| Color of compound (with titanium dioxide) | Equal to smoked sheet | Whiter than pale crepe | Light brown | Equal to smoked sheet |
| Discoloration on exposure to U.V. lamp (48 hrs.) | Equal to smoked sheet | Deep yellow-brown | Dark brown | Cream, less than pale crepe |

main object is to keep the mix as simple as possible, thus:—pale crepe rubber, 100; zinc oxide, 10; blanc fixe, 75; stearic acid, 1.

In assessing the staining tendencies of antioxidants, etc., the accelerator system is naturally kept constant and a good nonstaining type, such as tetramethylthiuram monosulfide, is used. Whether a small quantity of titanium dioxide is added or not is rather a matter of personal choice. As already indicated, it can mask certain small effects, but it is useful in offsetting small variations in the color of the rubber itself, and also gives a good white background against which any discoloration can develop.

*Fillers.*—In general, mineral fillers have little or no effect on the discoloring of rubber compounds, though naturally some fillers give much better whites than others because of their superior pigmentary properties. A mix that is slightly transparent will look drab beside one containing an opaque filler, such as titanium dioxide.

Fillers with high pigmentary power can also effectively mask the coloration and discoloration caused by some other ingredient of the mix, which would be immediately evident if a less powerful white filler were used. This may give the impression that titanium dioxide discolors less on exposure to light than other fillers, such as whiting or barytes, whereas, in fact, this is not true.

Usually coloration associated with mineral fillers is due to impurities, such as lead or iron, which form dark colored sufides on cure[4]. This source of coloration is more important with fillers than with other ingredients of a mix, since the former are used in comparatively high proportions.

*Sulfur.*—Besides the ability of sulfur to form dark sulfides by reaction with other ingredients, it can also react with external materials, notably silver and copper. In cable making, the effect of the rubber insulant on a poorly tinned copper wire is too well known to need further elaboration.

## ACCELERATORS

The coloration and discoloration due to accelerators is to some extent relative, and whether an accelerator is described as staining or not depends on the standard one adopts. Mercaptobenzothiazole is quoted in most trade literature as being nonstaining, whereas in fact it both colors and discolors to a small degree. Nevertheless, mercaptobenzothiazole can be taken as a standard, and those accelerators which stain less than this can be described as nonstaining, while those that stain more can be regarded as staining types.

*Coloration.*—Confining the discussion for the moment to the coloration of the rubber compound, it is true to say that, in general, the higher the speed of the accelerator the less the coloration. Thus, guanidines, aldehydeamines and thiocarbanilides color the compound, whereas thiurams, dithiocarbamates and xanthates give minimum coloration, the thiazoles being intermediate. Zinc isopropylxanthate probably gives the least coloration of all, but its use is naturally limited to proofings and to room temperature cures. There is little difference between the thiurams and the dithiocarbamates in compounds containing the usual amounts of sulfur, but sulfurless thiuram vulcanizates have a distinct yellow cast, especially on undercures. (See Figure 1 and Table 3).

The statement that the faster the accelerator the less the coloration should not be taken too literally, however, as among the aldehydeanimes, butyraldehydeaniline condensate and ethylidineaniline condensate give dark brown vulcanizates, whereas the much slower accelerator formaldehyde-*p*-toluidine condensate gives a yellow brown. Thiocarbanilide, another very slow accelerator, also colors less than the first two aldehydeamines mentioned.

Accelerators containing lead, such as lead pentamethylenedithiocarbamate, give brown vulcanizates due to the formation of lead sulfide.

*Effect of cure on coloration.*—State of cure, as well as the amount of accelerator used, has a marked effect on the color of the vulcanizate. In general, compounds containing coloring accelerators darken with cure, full coloration occurring at technical optimum. With some accelerators overcure causes further darkening, notably with the slower aldehydeamines, where technical optimum, as indicated by the development of tensile strength, is not always easy to judge. Gross undercures of all accelerators may have a pale yellow tint, probably due to unreacted sulfur.

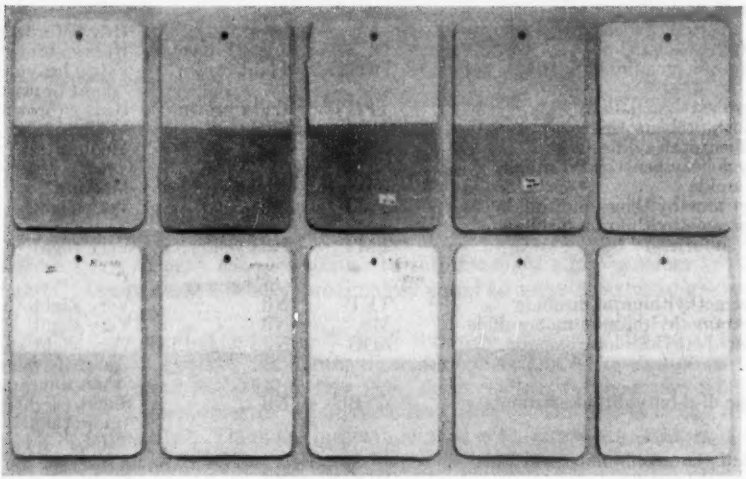

FIG. 1.—Coloration and discoloration of accelerators. Top half of each specimen shows coloration; bottom half shows discoloration after exposure to U.V. light for 48 hrs.

*Left to right, top* (1) thiocarbanilide
(2) formaldehyde-*p*-toluidine
(3) butyraldehydeaniline
(4) diphenylguanidine
(5) mercaptobenzothiazole
*Bottom* (6) tetramethylthiuram disulfide
(7) tetramethylthiuram disulfide (sulfurless)
(8) tetramethylthiuram monosulfide
(9) zinc diethyldithiocarbamate
(10) zinc isopropylxanthate

The development of the brown color by some of the aldehydeamine accelerators during cure can be very sudden. The undercures of butyraldehydeaniline are practically free from coloration, the brown color developing rapidly just before optimum cure is reached. This change is even more remarkable with the reaction product based on ammonia, formaldehyde, and ethyl chloride (Figure 2).

*Discoloration.*—With accelerators, discoloration runs closely parallel with coloration; that is to say, the faster accelerators discolor less in general than the slow ones (see Figure 1 and Table 3).

The thiurams as a class give the minimum discoloration and, of the accelerators tested in this work, tetramethylthiuram monosulfide is possibly the best. Sulfurless thiuram compounds are also remarkably free from discoloration.

TABLE 3

COLORATION AND DISCOLORATION DUE TO ACCELERATORS

| Name | Abbreviation | Coloration | Discoloration |
|---|---|---|---|
| Thiocarbanilide | TC | Slight | Very heavy (brown) |
| Formaldehydeaniline condensate | MA | Yellow-brown | Very heavy (orange-brown) |
| Formaldehyde-*p*-toluidine condensate | MT | Yellow-brown | Very heavy (orange-brown) |
| Ethylidineaniline condensate | RN | Dark brown | Very heavy (dark brown) |
| Butyraldehydeaniline condensate | BA | Dark brown | Heavy (brown) |
| Formaldehydeammonia-ethyl chloride condensate | — | Brown | Heavy (brown) |
| Diphenylguanidine | DPG | Light brown | Heavy (brown) |
| Di-*o*-tolylguanidine | DOTG | Light brown | Fairly heavy (light brown) |
| Triphenylguanidine | TPG | Light brown | Heavy (brown) |
| Mercaptobenzothiazole | MBT | Slight | Medium |
| Dibenzothiazyldisulfide | MBTS | Slight | Medium |
| Cyclohexylbenzthiazyl sulfenamide | HBS | Slight | Medium |
| Tetramethylthiuram disulfide | TMT | Nil | Very slight |
| Tetramethylthiuram disulfide (sulfurless) | TMT | Pale yellow, esp. on undercures | Very slight |
| Tetraethylthiuram disulfide | TET | Nil | Very slight |
| Tetramethylthiuram monosulfide | MS | Nil | Very slight |
| Zinc diethyldithiocarbamate | ZDC | Nil | Very slight (slightly more than thiurams) |
| Zinc di-*n*-butyldithiocarbamate | ZNBC | Nil | Slight (slightly more than ZDC) |
| Diethylammoniumdiethyl dithiocarbamate | DDCN | Nil | Slight (slightly more than ZDC) |
| Zinc isopropylxanthate | ZIX | Nil | Very slight |
| Vulcafor-DAW | DAW | Slight | Medium (equal to thiazoles) |
| Vulcafor-F | F | Slight | Medium (equal to thiazoles) |
| Vulcafor-FN | FN | Slight | Medium (equal to thiazoles) |
| Vulcafor-DAU | DAU | Nil | Very slight (equal to ZDC) |
| Vulcafor-DHC | DHC | Nil | Slight (slightly more than ZDC) |

The excellent result obtainable with tetramethylthiuram monosulfide demonstrates also that coloration and discoloration are independent of the color of the accelerator. This product is a bright yellow powder, and uncured stocks containing it have a pale lemon tint, yet its vulcanizates are free from coloration and give minimum discoloration. Diphenylguanidine, on the other hand, is a white powder, yet colors and discolors rubber compounds to a considerable degree.

Of the dithiocarbamates, zinc diethyldithiocarbamate discolors less than

diethylammonium diethyldithiocarbamate, despite the fact that the latter is the faster accelerator.

In the past, di-*o*-tolylguanidine has often been described as staining less than diphenylguanidine, and has been preferred for this reason. By modern standards, however, di-*o*-tolylguanidine is a staining accelerator, so any advantage it has in this respect over diphenylguanidine is only relative.

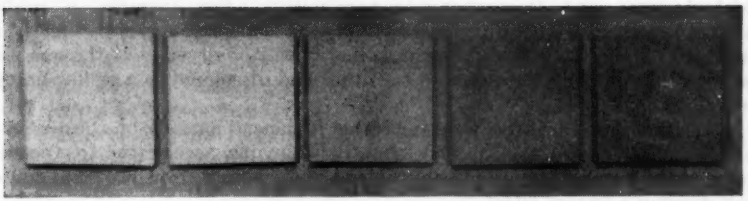

FIG. 2.—Effect of cure on coloration.

*Left to right* (1), (2), (3) undercures
(4) technical optimum cure
(5) overcure

The coloration and discoloring properties of the delayed-action accelerators, Vulcafors DAW, F and FN, are similar to the thiazoles, and Vulcafors DAU and DHC may be regarded as approximately equal to zinc diethyldithiocarbamate in this respect.

*Effect of cure on discoloration.*—State of cure also affects the degree of discoloration and, in general, maximum discoloration occurs at optimum cure. Undercures are often remarkably free from discoloration, for example, mixes accelerated with guanidines or aldehydeamines, despite the fact that the full cures discolor heavily. There are indications that with faster accelerators discoloration falls off with overcure (Figure 3). This has been particularly noticed with specimens exposed to the U.V. light. It is not so noticeable with the slower accelerators, as the depth of the discoloration is masked by the coloration of the vulcanizate.

An interesting observation has been recorded by Defries and Naunton[5]. If part of an uncured rubber mix is exposed to light, little or no effect is evident,

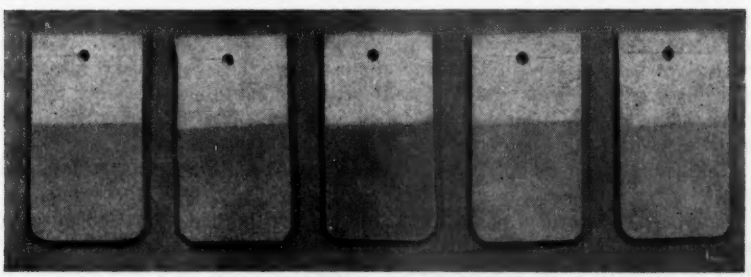

FIG. 3.—Effect of cure on discoloration. The bottom half of each specimen has been exposed to U.V. lamp for 48 hrs.

*Left to right* (1) and (2) undercures
(3) technical optimum cure
(4) and (5) overcures

but on cure the portion that has been exposed is more colored than the remainder. This is due to slight surface vulcanization of the portion exposed, so that it becomes overcured, and consequently more colored, on normal cure. The effect depends on the degree of coloration associated with the accelerator employed.

The authors have already commented on the bleaching action of light in the early stages of exposure, this effect being especially noticeable with guanidine, aldehydeamine and thiocarbanilide accelerators. For example, a rubber sample, accelerated with diphenylguanidine, had one side exposed directly to sunlight and the other side facing a wall. It was observed that the one side had been bleached by the sun, and the other had discolored to a yellow-orange color.

*Finger marking.*—Finger marking seems to depend entirely on the accelerator used, and its form may vary slightly from one accelerator to another. Usually, the finger mark, almost invisible at first, rapidly turns brown and later may develop a bronze effect.

As a general guide, it is true to say that finger marking occurs with only the faster accelerators and, as a class, the thiurams, including sulfurless tetramethylthiuram disulfide cures, are particularly prone to exhibit this defect. The dithiocarbamates are only slightly better, but mixes accelerated with thiazoles, guanidines, and aldehydeamines seem immune from finger marking.

Of the ultra-accelerators, Vulcafor-DHC seems to be the best for resisting this form of staining, which can often completely spoil the appearance of an otherwise attractive article.

Finger marking is not necessarily due to dirty hands on the part of the operator, though it can certainly be accentuated by the presence of traces of copper, such as normally contaminate the fingers through the handling of coins. Neither is it due to perspiration, as finger marking occurs when rubbers are handled with freshly washed hands. It is independent of the state of cure and is most likely to occur immediately after the hot article is removed from the mold.

*Selenium and tellurium.*—Selenium and tellurium are both employed as secondary accelerators. The former imparts a yellow-green shade to the vulcanizate, and tellurium colors the compound a pale gray.

On exposure to light, selenium causes very heavy discoloration, the rubber turning a bright pink. Even the flash which protrudes from the mold has been observed to turn pink during cure. The discoloration seems, however, to depend to some extent on the primary accelerator. With mixes accelerated primarily with tetramethylthiuram monosulfide, the pink discoloration described above has been observed, but with mercaptobenzothiazole mixes a bright yellow discoloration has developed first, becoming pinkish on more prolonged exposure.

Tellurium discolors only slightly, the compound turning a medium gray color.

*Retarders.*—Retarders of the weak organic acid type, such as salicylic acid, benzoic acid, phthalic anhydride and diphenylguanidine oxalate, have little effect on coloration and discoloration. Sodium acetate, used as a retarder for Neoprene stocks, discolors slightly.

*N*-Nitrosodiphenylamine, however, imparts a yellow color to the vulcanizate and causes fairly heavy discoloration on exposure to light.

## ANTIOXIDANTS

As the range of materials having antioxidant properties is so wide, an attempt has been made to systematize this part by investigating a number of representative types, given here by their chemical names.

(1) Rubber compound without antioxidant
(2) Nonstaining antioxidant
(3) *sym.* Di-β-naphthyl-*p*-phenylenediamine
(4) Polymerized trimethyldihydroquinoline
(5) Acetonediphenylamine reaction product
(6) Aldolnaphthylamine (powder)
(7) Aldolnaphthylamine (resin)
(8) Phenyl-α-naphthylamine
(9) Phenyl-β-naphthylamine
(10) Flex-cracking antioxidant.

In the experimental work, the antioxidant was added in the proportion of one part per 100 parts of rubber, with the standard base mix as previously described. The accelerator used was tetramethylthiuram monosulfide.

One of the difficulties in selecting the list given above is that antioxidants are for the most part complicated chemicals, and there can be no guarantee that the product made by one firm is exactly the same in its chemical constitution and its behavior as ostensibly the same product made by another firm. This is

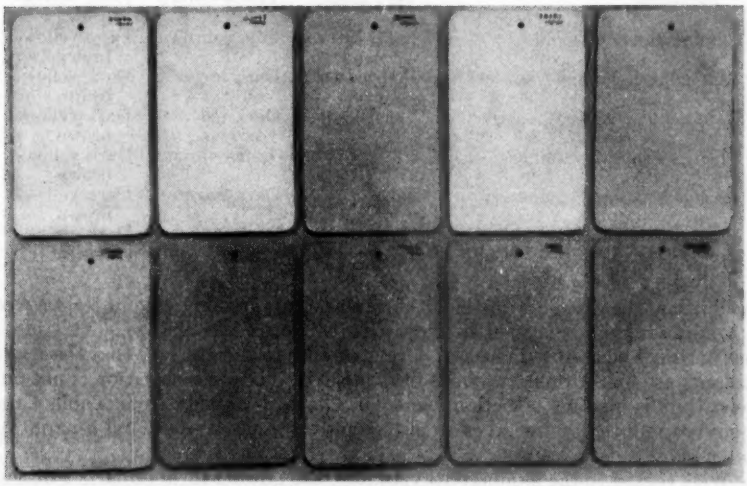

FIG. 4.—Discoloration due to antioxidants.

*Left to right, top* (1) compound without antioxidant
(2) nonstaining antioxidant
(3) *sym.* di-β-naphthyl-*p*-phenylenediamine
(4) polymerized trimethyldihydroquinoline
(5) acetonediphenylamine
*Bottom* (6) aldolnaphthylamine (powder)
(7) aldolnaphthylamine (resin)
(8) phenyl-α-naphthylamine
(9) phenyl-β-naphthylamine
(10) flex-cracking antioxidant

particularly the case with condensation products. It will be seen that, with regard to aldolnaphthylamine condensate, both the powder and the resin forms are listed, and important differences between them will be indicated below.

Several antioxidants have been found to be completely nonstaining in all the applications studied. Of these, Nonox-NS, Nonox-NSN, and a polyalkylated phenol sulfide may be mentioned, though the actual example used in this work was the new nonstaining antioxidant, Nonox-EX.

In dealing with antioxidants, a distinction should again be made between coloration and discoloration, for a number of antioxidants discolor but do not color and some color yet discolor only slightly. For example, the two phenylnaphthylamines are virtually free from coloration, yet their ultimate discoloration of the rubber compound is very heavy indeed (see Table 4 and Figure 4).

TABLE 4

COLORATION AND DISCOLORATION DUE TO ANTIOXIDANTS

| | Coloration | Discoloration (3 weeks' daylight) | Discoloration (48 hrs. U.V.) |
|---|---|---|---|
| Compound without antioxidant | Nil | Nil | Pale yellow |
| Nonstaining antioxidant (Nonox-EX) | Nil | Nil | Pale yellow |
| *sym.* Di-β-naphthyl-*p*-phenylenediamine | Dove gray | Gray | Mottled gray-yellow |
| Polymerized trimethyldihydroquinoline | Very slight | Yellow-brown | Deep yellow-brown |
| Acetonediphenylamine | Light brown tinge | Yellow-brown | Deep yellow-brown |
| Aldolnaphthylamine (powder) | Red-brown tinge | Dark brown | Dark yellow-brown |
| Aldolnaphthylamine (resin) | Very slight | Dark red-brown | Dark yellow-brown |
| Phenyl-α-naphthylamine | Nil | Orange-brown | Dark yellow-brown |
| Phenyl-β-naphthylamine | Nil | Dark brown | Dark yellow-brown |
| Flex-cracking antioxidant | Gray | Dark gray-brown | Dark gray-brown |

In addition, the discoloration is not developed very quickly, and at least a week in bright sunlight is needed to show a really noticeable change. This means that one may be tempted on short-term exposure tests to believe that these antioxidants are nonstaining, whereas in fact the ultimate discoloration is not only heavy but is also an objectionable color. It will be seen from Table 4 that phenyl-α-naphthylamine gives an orange brown shade, and phenyl-β-naphthylamine gives a dark brown.

With regard to the aldolnaphthylamines, the powder form imparts a distinct red-brown color to the vulcanizate, while the resin colors only slightly. On exposure to light, however, both discolor heavily, the powder giving a dark brown discoloration and the resin a dark red-brown.

The acetonediphenylamine condensate is interesting because, although it imparts a light brown coloration, this does not darken much on exposure to light, and the final effect is not nearly so objectionable as that due to some of the other antioxidants. Consequently, both this antioxidant and polymerized trimethyldihydroquinoline, which also only discolors to a light shade of yellow

brown, find applications where slight discoloration is permissible, especially as the stain is not readily communicated to other materials, though of this aspect more details are given below.

*sym*-Di-β-naphthyl-*p*-phenylenediamine gives a dove-gray vulcanizate and discolors fairly rapidly to a medium shade of gray. This, too, can be used in applications where a certain amount of discoloration can be tolerated.

Attention is drawn to the shades of these discolorations, as they are characteristic of the antioxidants, and will be seen again in various guises under staining by migration.

The development of the discoloration is considerably accelerated under the U.V. lamp and, as already indicated, this method of test is invaluable for rapidly assessing the nondiscoloring class of antioxidant. Nevertheless, the yellow stain which occurs on all vulcanizates under the U.V. lamp does modify the characteristic shades observed under ordinary daylight.

It may be argued that the antioxidants should have been added in proportions relative to their antioxidant strength, and that certain of them would have appeared better than indicated here if they had been incorporated in smaller yet sufficient amounts. It is, however, almost impossible to decide what proportions to add on such a basis and, furthermore, reduction in the quantity of antioxidant does not proportionately decrease the degree of discoloration. This is clearly shown by Figure 5, where a reduction in the amount of *sym*. di-β-naphthyl-*p*-phenylenediamine from 1 to 0.25 per cent (based on the rubber content of the mix) caused insignificant reduction in the degree of discoloration.

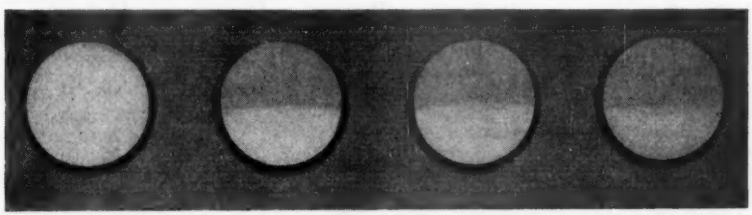

FIG. 5.—Effect of reducing proportion of antioxidant. (*sym*. di-β-naphthyl-*p*-phenylenediamine.) Per cent of antioxidant (based on rubber content) left to right: (1) nil, (2) 0.25 per cent, (3) 0.5 per cent, (4) 1 per cent.

Antioxidants are also added to raw rubber, *e.g.*, in the preparation of raw rubber-wax mixtures for the impregnation of paper and cardboard, and here coloration is just as important as discoloration (Table 5).

In passing, it may be mentioned that *sym*. di-β-naphthyl-*p*-phenylene diamine gives a pink color in hot paraffin wax and gray in cold. This color change is noticed to some extent in rubber also, but it is the gray shade which develops on exposing the cured rubber compound to light.

## OTHER COMPOUNDING INGREDIENTS

*Softeners.*—Softeners are another source of staining, and in this connection reference is made to a publication of some years ago[6]. In this, pine tar, coumarone resin and hardwood pitch were described as causing coloration of a serious character, whereas petroleum jelly, mineral oil, wool fat and palm oil gave a slight coloration; stearic acid, oleic acid, and castor oil were noted as giving the least coloration.

In the present work it has been found that coloration and discoloration are most likely to occur due to the use of various petroleum and coal tar residues, of indeterminate composition, which are offered to the trade from time to time. This is demonstrated to some extent by Table 6. This shows the coloration and discoloration caused by a range of typical softeners, which have been added in the proportion of 5 per cent on the rubber content of the mix.

TABLE 5

STAINING OF RAW RUBBER AND PARAFFIN WAX BY ANTIOXIDANTS

| | Pale crepe | | Paraffin wax | |
|---|---|---|---|---|
| Antioxidant | Coloration | Discoloration | Solubility | Coloration |
| Nonstaining antioxidant (Nonox-NS, Nonox-NSN) | Nil | Nil | Insoluble | Nil |
| Polyalkylated phenol sulfide | Nil | Nil | Soluble | Dark brown |
| *sym.* Di-β-naphthyl-*p*-phenylenediamine | Pink-purple gray | Darkens | Disperses as fine suspension | Gray (cold), pink (hot) |
| Polym. trimethyldihydroquinoline | Brown | Darkens | Slightly soluble | Yellow-brown |
| Acetonediphenylamine | Dark brown | Darkens | Slightly soluble | Brown |
| Aldolnaphthylamine (powder) | Dark red | Darkens | Disperses as fine suspension | Dark red |
| Aldolnaphthylamine (resin) | Nil | Darkens considerably | Insoluble | Nil |
| Phenyl-α-naphthylamine | Nil | Darkens considerably | Soluble | Pale pink |
| Phenyl-β-naphthylamine | Slight darkening | Darkens considerably | Soluble | Pale orange |
| Flex-cracking antioxidant | Dark brown | Darkens considerably | Partially soluble | Yellow brown |

Softeners such as petroleum jelly, liquid paraffin and paraffin wax have no ill effects, but the darker colored waxes, such as the ozokerite type, may cause a certain amount of coloration and discoloration, as do large additions of stearic acid. Light coumarone resin has only a slight deleterious effect, though serious discoloration has been observed when darker grades have been employed. Pine tar colors the vulcanizate badly.

Of other ingredients, plasticizers, based on mixtures of sulfonated petroleum products and butyl alcohol, are free from staining, as are peptizing agents of the thio-β-naphthol type. These materials are, of course, used in much smaller proportions than is usual for softeners, 2 per cent of plasticizer and 0.25 per cent of peptizer being typical additions.

*Rubber substitutes.*—Except for white factice, which does not color the mix and may, in fact, improve its whiteness, the use of rubber substitutes and reclaim darkens the color of the rubber compound and increases the tendency to discolor on exposure to light. Victoria factice colors only slightly, but Whitbro substitute and brown factice both impart a brown color. All increase the degree of discoloration (see Table 7).

The risk with using drab reclaim is that it may contain a trace of some staining ingredient. The reclaim used in the example quoted here, however, caused little increase in discoloration, though it did darken the color of the mix.

Substantial additions of whole-tire reclaim and mineral rubber, of course, give black compounds.

TABLE 6

COLORATION AND DISCOLORATION DUE TO SOFTENERS

Base mix

| | | | |
|---|---|---|---|
| Pale crepe | 100 | Sulfur | 2.5 |
| Zinc oxide | 10 | Vulcafor-MS | 0.5 |
| Blanc fixe | 75 | *Softener | 5 |
| Stearic acid | 1 | | |

* Except for peptizer and plasticizer where 0.25 part of the former and 2 parts of the latter were incorporated.

| Ingredient | Coloration | Discoloration |
|---|---|---|
| Control (no softener) | — | Pale yellow |
| Peptizer (thio-β-naphthol type) | As control | As control |
| Plasticizer (sulfonated petroleum product) | As control | As control |
| Petroleum jelly | As control | As control |
| Liquid paraffin | As control | As control |
| Paraffin wax | As control | As control |
| Stearic acid | Slight coloration | Slightly darker than control |
| Ozokerite type wax | Slight coloration | Slightly darker than control |
| Light coumarone resin | Slight coloration | Slightly darker than control |
| Petroleum residue | Slight coloration | Darker than control |
| Coal tar residue | Brown | Discolored considerably |
| Pine tar | Dark brown | Darker than control |

*Blowing agents.*—The common blowing agents, sodium bicarbonate and ammonium carbonate, definitely cause a darkening of the color of the resultant compound, though excellent white and colored sponges can be obtained as long as there is sufficient white filler to offset the coloration.

Of the organic blowing agents that have been introduced to the industry in the last few years, Vulcacel-BN gives no coloration or discoloration, and excellent whites and brilliant colors are possible with its use. Very similar is the American blowing agent based on dinitrosopentamethylenetetramine. The German Porofor-N, αα'-azo-di-isobutyronitrile, also gives excellent white sponges.

Diazoaminobenzene, however, is well known for the orange color it imparts to vulcanizates and for its ability to pass on this color to other materials that may come in contact with sponge articles made with it.

In general, antioxidants behave in sponge rubber with regard to their staining characteristics as one would expect from a knowledge of their behavior in normal rubber compounds. A notable exception, however, is *sym*-di-β-naphthyl-*p*-phenylenediamine, which, in sponge blown with Vulcacel-BN, not only imparts a brown color to the mix, but causes the rapid formation of a dark brown discoloration on exposure to light.

## STAINING BY MIGRATION

Staining by migration can take place not only from rubber to rubber but to many other materials, some a long way removed from the rubbery state. The fact that this form of staining can take place has been known in some spheres of the industry for many years, and some extraordinary examples have been quoted, but the results have never been set out in systematic fashion. In this section, various aspects are presented in an endeavor to clarify the problem so that it may be more readily recognized than hitherto.

Staining by migration is due, for the most part, to antioxidants, and to illustrate the various aspects selected, reference is made to the same antioxidants as were listed earlier.

*Cellulose acetate lacquers.*—Staining of cellulose acetate lacquers is of paramount importance to the electric cable manufacturer, as rubber insulated cables, taped, braided with cotton or genappe, and lacquered overall are ex-

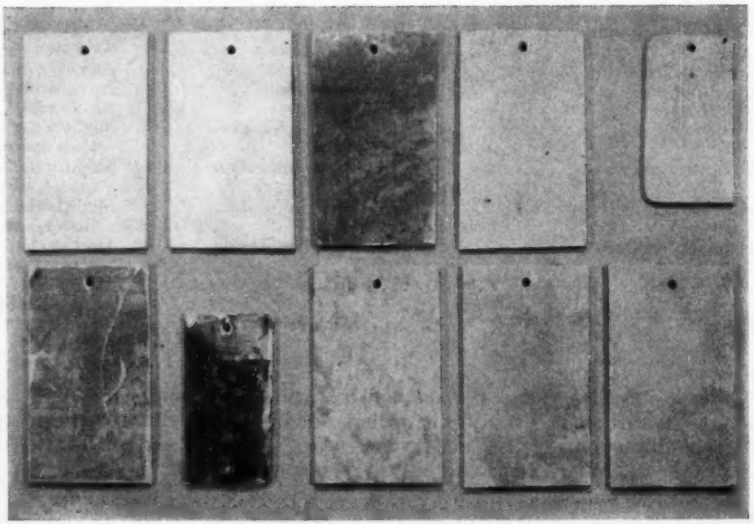

FIG. 6.—Staining by migration of cellulose acetate lacquers.

*Top*
(1) compound without antioxidant
(2) nonstaining antioxidant
(3) *sym.* di-β-naphthyl-*p*-phenylenediamine
(4) polymerized trimethyldihydroquinoline
(5) acetonediphenylamine

*Bottom*
(6) aldolnaphthylamine (powder)
(7) aldolnaphthylamine (resin)
(8) phenyl-α-naphthylamine
(9) phenyl-β-naphthylamine
(10) flex-cracking antioxidant

tensively used for switchboard wiring, etc. The colored braid, which may be all of one color though more usually of two colors, in wasp, striped or spotted pattern, shows through the transparent lacquer finish so as to make it easy to identify and follow any circuit in a multicircuit system. If the lacquer loses its clarity in storage or service, the cable becomes useless and if the wiring has already been completed a considerable expenditure in time and money is inevitable.

It is possible for antioxidants to migrate from the rubber insulant through the braid and into the cellulose lacquer and, if the antioxidant is a staining one, the lacquer itself will become stained and lose its clarity.

Figure 6 shows the result of coating rubber compounds containing the antioxidants listed above with a cellulose acetate lacquer. The coated samples were left overnight in a drawer and then exposed to ordinary sunlight. By the end of the day the staining was already visible in the more pronounced cases. About a week is necessary to distinguish between a real nonstaining antioxidant and those that only stain slightly.

That the stain is in the lacquer and not on the surface of the rubber underneath can be readily demonstrated by peeling off the lacquer film and showing that the rubber is virtually undiscolored.

The color of the various stains is most interesting as they line up with the discolorations produced on the rubber compounds already illustrated, though they are very much brighter in intensity. The colors are given in Table 8.

It will be seen that polymerized trimethyl dihydroquinoline and acetone-diphenylamine condensate give only a light brown staining. This renders these antioxidants very useful in the cable industry, for their value purely as antioxidants is generally acknowledged.

There is no necessity to use the U.V. lamp for accelerating this type of staining, as the colors appear rapidly in ordinary sunlight. Indeed, the U.V. lamp spoils the effect, as the lacquer itself turns a yellow color after a few hours under this treatment. There is, however, an interesting effect that may be observed with the U.V. lamp. When the lacquer coated samples containing phenyl-$\alpha$-naphthylamine, phenyl-$\beta$-naphthylamine and aldolnaphthylamine are placed under the U.V. lamp, a blue fluorescence appears in the lacquer. This persists for a few minutes, but gradually disappears as the staining develops: the stain with these antioxidants develops exceedingly rapidly under the U.V. lamp.

The addition of antioxidants direct to the lacquer and then exposing the dried film to light is not be be recommended as a method of assessing staining, as the natural color of the antioxidant so colors the lacquer that any change due to exposure to light is often difficult to see.

It has been suggested that with regard to lacquered cable the antioxidant may possibly be transferred to the lacquer from the rubber by the solvent action of the acetone in the thinners, and that the staining could be prevented by using an antioxidant insoluble in acetone. This, however, is a fallacy, since the antioxidant can migrate easily into the dried lacquer film without the use of thinners. In any case, most antioxidants are soluble in acetone or are readily dispersible, and they are similarly soluble or readily dispersible in the plasticizers commonly used in the manufacture of cable lacquers.

The obvious solution to the problem is to use a nonstaining antioxidant, such as are already offered to the trade. But one should guard against those antioxidants which stain only slightly in rubber, for their effect in this applica-

TABLE 8

STAINING BY MIGRATION OF ANTIOXIDANTS FROM RUBBER COMPOUND TO OTHER MATERIALS

| Antioxidant | Color of stain | | | | |
|---|---|---|---|---|---|
| | Cellulose acetate lacquer | Nitrocellulose enamel | Vulcaprene varnish | Black-out varnish | P.V.C. |
| Compound containing no antioxidant | Nil | Nil | Nil | Nil | Nil |
| Nonstaining antioxidant (Nonox-EX) | Nil | Nil | Nil | Nil | Nil |
| *sym.* Di-β-naphthyl-*p*-phenylenediamine | Purple | Gray patches | Dark blue-gray | Pale gray | Dark blue-gray |
| Polymerized trimethyl dihydroquinoline | Light brown | Practically nil | Fawn | Light brown | Practically nil |
| Acetonediphenylamine condensate | Light brown | Practically nil | Fawn | Light brown | Practically nil |
| Aldolnaphthylamine (powder) | Brown | Practically nil | Pale mauve | Light brown | Pale brown |
| Aldolnaphthylamine (resin) | Red-brown | Brown | Dark red | Red-brown | Red-brown |
| Phenyl-α-naphthylamine | Orange | Orange | Orange-pink | Orange-brown | Orange-yellow |
| Phenyl-β-naphthylamine | Red-brown | Mottled purple | Purple | Dark gray | Orange-mauve |
| Flex-cracking antioxidant | Gray-brown | Dark brown | Gray-green | Green; darkening to dark gray | Gray-brown |

tion may be unexpectedly pronounced. The two slightly staining antioxidants already mentioned (namely, polymerized trimethyldihydroquinoline and the acetonediphenylamine condensate) can, however, be used without much risk.

In general, accelerators have no effect on this type of staining, though a very faint yellow stain, which does not seem to develop further on prolonged exposure to light, has been noticed with sulfurless tetramethylthiuram disulfide cures. The slower aldehydeamines should also be used with caution. Selenium and tellurium do not cause staining of the lacquer.

*Nitrocellulose enamels.*—White nitrocellulose finishes are used on the panels of domestic appliances, such as refrigerators, cookers, washing machines and the like. Rubber is an integral part of these appliances and finds employment in gaskets, hose, cables, etc., so it is most important that there should be no staining from the rubber to the enamels in service to impair their clean and pleasing appearance.

TABLE 7

COLORATION AND DISCOLORATION DUE TO RUBBER SUBSTITUTES, ETC.

Base mix, etc.

| | | | |
|---|---|---|---|
| Pale crepe rubber | 100 | Sulfur | 2.5 |
| Zinc oxide | 10 | Vulcafor-MS | 0.5 |
| Blanc fixe | 75 | Substitute | 10 |
| Stearic acid | 1 | | |

N.B.—In the mix containing white factice, 10 parts of magnesium oxide was also added.

| Ingredient | Coloration | Discoloration |
|---|---|---|
| Control | — | Pale yellow |
| White factice | As control | Yellow-brown |
| Victoria factice | Slightly darker | Yellow-brown |
| Whitbro substitute | Brown | Brown |
| Brown factice | Brown | Yellow-brown |
| Drab reclaim | Gray | Yellow-brown |
| Whole tire reclaim | Black | — |
| Mineral rubber | Black | — |

The method of test adopted is to place the rubber compounds on an enamelled panel, cover with a sheet of paper or cardboard, and apply pressure by means of lead weights. The assembly is then placed in an oven at 70° C for four days to accelerate any migration of rubber chemical from the rubber to the enamel. After this treatment, the enamel may be stained slightly or perhaps not at all, but when the panel is subsequently exposed to sunlight, the more pronounced staining becomes brightly visible within a few hours. The effect is so rapid that again the U.V. lamp is not necessary, except perhaps to distinguish between nonstaining compounds and those that only stain slightly after prolonged exposure. The U.V. lamp also tends to dull the colors so that the various characteristic shades are not so well distinguished.

It is, of course, antioxidants which are the chief offenders in this type of staining, and it will be seen from Table 8 that the bright orange of phenyl-$\alpha$-naphthylamine and the mottled purple effect of phenyl-$\beta$-naphthylamine are similar in color to the stains produced on cellulose acetate lacquers.

A curious anomaly is aldolnaphthylamine powder, which in this instance is nonstaining, whereas aldolnaphthylamine resin imparts a heavy brown stain. This would appear to be due to the different physical forms of the two types, the powder form having a lower mobility than the resin in the hard enamel finish. With nitrocellulose lacquers, however, both forms cause staining by migration.

*sym*-Di-β-naphthyl-*p*-phenylenediamine also gives an unusual effect. At first sight, it appears to be absolutely nonstaining, but a closer inspection of the panel reveals here and there small patches of the characteristic dark gray stain of this antioxidant. In a number of experiments on these lines with various brands of enamels, these small patches of gray stain have developed in practically every case. Again, the phenomenon is difficult to explain, for the gray stain appears so evenly over the surface in every other application studied that there can be no question of poor dispersion of the antioxidant.

It will be noticed that polymerized trimethyldihydroquinoline and acetonediphenylamine are practically free from staining.

Accelerators seem to have a more pronounced effect on the staining of these enamels than on cellulose acetate lacquers, though the initial perfect whiteness of the enamels makes slight changes in color much more readily discernible than is possible with transparent films. Guanidines, such as diphenylguanidine, and sulfurless tetramethylthiuram disulfide cures give pale yellow-orange stains. Aldehydeamines are also suspect, butyraldehydeaniline cures, for example, giving a pale yellow-brown stain. The thiazoles, mercaptobenzothiazole and dibenzthiazyl disulfide, give a very faint stain under the accelerated test employed, but may be regarded essentially as nonstaining. The thiurams in normal sulfur mixes and the dithiocarbamates are perfectly free from staining.

The majority of the softeners used in rubber compounds do not cause staining, though very slight staining has been experienced with such softeners as pine tar.

It may be mentioned that the staining due to accelerators and softeners, in contrast to that caused by antioxidants, is evident on the enamel when the panel is removed from the oven, and is not materially increased by subsequent exposure to light.

With regard to the enamels themselves, some darken slightly on their own account during the period in the oven, and this should be allowed for in the assessment of results. In general, matt finish enamels are stained more readily than those having a high gloss.

There are other instances besides nitrocellulose enamels, where nitrocellulose may come in contact in service with rubber. Nitrocellulose lacquers are used in the proofing industry in conjunction with rubberized fabrics, for example, in the production of leathercloth, and staining by migration, similar to that described here, can readily take place.

*Urea-formaldehyde resin enamels.*—These appear to behave in the same way as the nitrocellulose enamels.

*Vitreous enamels.*—No staining of vitreous enamels due to the migration of antioxidants has been observed.

*Vulcaprene lacquers.*—A fairly recent development of rubber technology has been the production of finishes for rubber articles, which are as flexible as the rubber base itself. This means that a rubber article can be made with the physical properties to meet the most exacting needs yet can have a pleasing brightly colored appearance. So, as it is the appearance of these articles which is a major selling point, it is essential that they shall not be spoilt by staining due to the migration of chemicals from the underlying base.

Rubber compounds containing the antioxidants listed above were sprayed with a white finishing lacquer, based on the synthetic rubber, Vulcaprene, and then exposed to ordinary daylight. Within 24 hours the characteristic stains were brightly visible on the lacquer surface (Table 8).

Accelerators have little or no effect on the staining by migration of Vulcaprene lacquers, though again the sulfurless thiuram cures should be used with caution.

*Black-Out.*—Very similar to Vulcaprene lacquer in its application, but completely different in its constitution, is the American surface finish known as Black-Out. Despite its name, it can be obtained in a variety of colors, the white quality being used in the present work.

Results are essentially the same as those obtained with Vulcaprene lacquer, though the colors of the stains are different, notably with the flex-cracking antioxidant, which in the early stages of exposure gives quite an attractive shade of green (Table 8).

Here, as also with nitrocellulose enamels and polyvinyl chloride, the stain of aldolnaphthylamine powder is less pronounced than that of the resin.

These results with Vulcaprene and Black-Out lacquers mean that the finishes have to be used with extreme caution in one of the major outlets for which they have been suggested, namely, the sidewalls of tires. Sidewalls usually contain a flex-cracking antioxidant and, in every staining application examined, the well-known proprietary brands of flex-cracking antioxidants all stain badly.

*Wax finishes.*—Another class of finish that may be mentioned is the wax dispersion type which, when applied, consists essentially of a very thin layer of waxy material on the surface of the rubber to give it a better appearance.

Staining by migration can occur into this wax film in the same way as it can into surface lacquers with the production of similar characteristic colors.

The phenomenon in this case, however, is comparatively unimportant, for no attempt is being made to alter the color of the finished article, as the rubber is clearly visible through the wax film. With the lacquer finishes, on the other hand, the manufacturer is trying to cover up the undesirable color of the rubber by putting on a coating of a different color, so staining of lacquer is important.

*Polyvinyl chloride.*—Another form of staining by migration is from rubber to polyvinyl chloride. A particular example may occur in the manufacture of vulcanized india-rubber cable with a polyvinyl chloride sheath.

The problem is complicated somewhat by the fact that the sulfur in the rubber mix may also have an effect. Many polyvinyl chloride compounds contain lead as a stabilizer (for example, basic lead carbonate) and, under the influence of heat, such as may occur during the extrusion of the polyvinyl chloride sheath over the rubber insulated core, black lead sulfide may be formed at the interface.

This has been demonstrated by pressing together a sheet of already vulcanized rubber, containing about 1.3 per cent total sulfur on the mix, and a sheet of lead carbonate stabilized polyvinyl chloride at 141° C for 10 minutes. On stripping apart, both the rubber and the polyvinyl chloride were heavily stained with lead sulfide at the interface. This stain, of course, may not be visible in the finished article if the polyvinyl chloride layer is sufficiently thick and opaque, but it is mentioned because it is a complicating factor, where a fairly transparent polyvinyl chloride compound is used and where it can be mistaken for antioxidant stain.

The use of a sulfurless tetramethylthiuram disulfide mix to obviate this lead sulfide stain is not altogether successful. Not only is a small amount of lead sulfide formed, but there is also a yellow stain due to the comparatively large quantity of tetramethylthiuram disulfide.

The solution is to use a leadless polyvinyl chloride compound, stabilized, for example, with calcium stearate. When this is pressed together with a rubber compound under heat, the interface remains perfectly white.

Thiazoles, dithiocarbamates and thiurams (with normal sulfur) give no staining by migration, but sulfurless thiuram cures give the yellow stain previously described. Aldehydeamines, for example, butyraldehydeaniline, also give yellow staining at the interface.

Having now dealt with the complication of lead sulfide formation, it is pertinent to consider the effect of antioxidants. If a thin layer of polyvinyl chloride is placed over a rubber compound containing a staining antioxidant, and the assembly exposed to sunlight, staining of the polyvinyl chloride occurs in a few hours. Again the colors of the stains follow their usual trends, as is shown by Table 8.

*Paper and textiles.*—From the examples discussed so far, it is clear that staining due to the migration of antioxidant from rubber to other materials follows similar trends in all cases, so with regard to papers and textiles it is merely pointed out that antioxidants can stain by migration these materials also. The color of the stains produced is much as would be expected; for example, phenyl-$\beta$-naphthylamine gives a brown stain.

There is, however, a different form of staining of papers and textiles associated with rubber goods. This is the effect commonly known as pinking, which can occur, for example, on the white canvas duck uppers of rubber soled tennis shoes.

This pinking has been recognized in the cotton industry for many years and reference is made to the work carried out at the Shirley Institute[7]. The pink stain is due to aniline vapor contaminating the atmosphere, and it occurs on cotton material that has been bleached with hypochlorite in neutral or alkaline solution. Goods bleached in an acid liquor or with hydrogen peroxide appear to be immune from pink staining.

Further work[8] has shown that beside aniline the vapors of *ortho*- and *para*-toluidine and of $\alpha$-naphthylamine also cause pinking, whereas the vapors of methylaniline and *m*-phenylenediamine give mauve and cream staining respectively.

Of the chemicals which did not cause pinking, diphenylguanidine is listed. This is curious, as diphenylguanidine has long been suspected in the rubber industry as a cause of this effect, and in the present work this has been confirmed.

The pinking of paper and cotton goods is essentially the same phenomenon, and the view usually expressed with regard to paper[9] is that the stain is due to the reaction of aniline with lignocellulose. Consequently the quality of the paper or of the cotton has a profound effect on the likelihood of staining.

To simplify the experimental work, a particular type of white cardboard was chosen which was known to give positive results. The cardboard contained roughly 30 per cent chemical wood pulp, 65 per cent bleached straw and esparto and 5 per cent waste paper. Of the total, 25 per cent was china clay. It had been bleached with hypochlorite, and gave a positive reaction for the presence of lignocellulose. The method was simply to place rubber compounds containing various accelerators on sheets of the cardboard and to examine them at intervals by lifting off the rubber samples. Though the findings are confined to this cardboard, they may be accepted as being generally true. That is to say, if it is possible for a paper to pink by reason of its make-up and manufacturing treatment, then it will be stained by the same accelerators as caused pinking of the cardboard described above.

These experiments show that rubber compounds containing guanidines, aldehydeamines and thiocarbanilide all cause pinking when placed in contact with the cardboard. Of the guanidines, triphenylguanidine seems to be the worst offender, with diphenylguanidine next, and di-*o*-tolylguanidine least. Thiocarbanilide, formaldehydeaniline, formaldehyde-*p*-toluidine and ethylidineaniline all stain heavily, but no pinking has been observed due to butyraldehydeaniline.

It is also found that the intensity of the pink stain increases with the state of cure, being at a maximum with optimum and overcures. Undercures have a tendency to cause a yellow stain rather than a pink, and this is more noticeable with the aldehydeamines than with the guanidines.

A pronounced yellow stain occurs on paper in contact with rubber cured with sulfurless tetramethylthiuram disulfide. This does not come within the category of pinking, but is a case of staining by migration, as sulfurless tetramethylthiuram disulfide cures cause yellow staining in a number of the other applications previously mentioned.

TABLE 9

| Carbon black | Abbreviation | Staining of Vulcaprene lacquer | Staining of white enamel |
|---|---|---|---|
| Kosmink | CC | Very slight | Nil |
| Kosmobile-HM | MPC | Nil | Nil |
| Kosmos-60 | RF | Nil | Nil |
| Kosmos-20 | SRF | Nil | Nil |
| Acetylene black | — | Nil | Nil |
| Fine thermal black | FT | Serious | Serious |
| Medium thermal black | MT | Nil | Very slight |
| Lamp black | — | Nil | Slight |

NOTE.—It is impossible to reproduce exactly in a black and white photograph the various effects observed on the test-specimens. Consequently, the descriptions given in the tables may vary slightly in certain instances from the appropriate photographs.

The fact that the pink stain on the cardboard occurs underneath the rubber shows that the effect is independent of light, which is different from the other examples of staining by migration examined. If the cardboard is placed over the rubber, then pink staining still occurs, first on the surface in contact with the rubber and then permeating to the top surface of the cardboard. This means, for example, that a pair of tennis shoes may look perfectly satisfactory when packed in the factory, but may show pink staining of the canvas uppers or of the wrapper paper when they reach the customer.

*Carbon black.*—Carbon black is another possible source of staining by migration that has been mentioned from time to time, and one brand of carbon black is actually marketed in both staining and nonstaining forms[10]. In this instance, the phenomenon is of importance where white or colored lacquers are applied to the surface of black compounds or where the latter may come in contact with white enamels or with white rubbers.

Experiments have been carried out using tread type compounds containing approximately 25 volumes of carbon black (on the rubber) and examining their staining effect on Vulcaprene lacquers and on white enamelled panels.

In general, the staining due to carbon black is only very slight compared with that due to certain antioxidants, and the only black found to cause staining at all serious in character was a fine thermal grade. This has been observed

with both methods of test. Slight staining of enamels has also been experienced with medium thermal and lamp blacks. The channel and furnace types appear in general to be nonstaining (Table 9).

## REFERENCES

[1] *Vanderbilt News* **13**, No. 6 (1947); Murray and Watson, *Rubber Age* (London) **29**, 326 (1947); Moses and Rodde, *India Rubber World* **119**, 201 (1948).
[2] Sanders, RUBBER CHEM. & TECHNOL. **22**, 465 (1949).
[3] Baruth, *Rubber Age* (N. Y.) **63**, 52 (1948).
[4] Robertson, *Trans. Inst. Rubber Ind.* **4**, 190 (1928).
[5] Defries and Naunton, *Trans. Inst. Rubber Ind.* **4**, 298 (1929).
[6] Somerville, *Rubber Age* (N. Y.) **69**, 15 (1923).
[7] *Bulletin of the Shirley Institute* **7**, 16 (1934).
[8] *Bulletin of the Shirley Institute* **8**, 326 (1935).
[9] Naunton, *Trans. Inst. Rubber Ind.* **2**, 18 (1926); Discussion.
[10] *Vanderbilt News* **14**, No. 8 (1948).

# HAVE MECHANICAL STRESSES ANY EFFECT ON THE OXIDIZABILITY OF RUBBER?

JEAN LE BRAS AND ANDRÉ SALVETTI

INSTITUT FRANÇAIS DU CAOUTCHOUC, PARIS, FRANCE

The July 1949 issue of RUBBER CHEMISTRY AND TECHNOLOGY contains, on pages 690–698, a paper of the title above by Le Bras and Salvetti.

On page 693, the last sentence in the paragraph following Table 1 has a reference number 11 at the end. This refers, not to the paper by Moureu and Dufraisse given in the table of References, but to the following comments, which appeared in the original French text, but not in the translation in RUBBER CHEMISTRY AND TECHNOLOGY.

Tests have been carried out at the French Rubber Institute with mixtures of the same compositions as those used by Somerville, Ball and Cope[10]. Dumbbell test-specimens were employed, and the range of elongations was from 50 to 300 per cent. Aging tests in a Geer oven confirmed the results of Somerville, Ball, and Cope; the higher the elongation, the greater was the degradation. The total surface exposed, *i.e.*, of the narrow straight part of the test-specimen, does not change significantly with increase in elongation; on the contrary, the cross-section decreases, and for a given time of aging, there is a well-defined correlation between the changes in tensile strength and the changes in cross-section. This is explained by the diffusion of oxygen into the mass. These experiments were carried out by M. Le Foll, and the present authors wish to show their appreciation to him for his collaboration.

# PERMANENT SET IN VULCANIZED RUBBER

L. MULLINS

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

The October 1949 issue of RUBBER CHEMISTRY AND TECHNOLOGY contains, on pages 1036–1044, an article entitled "Permanent Set in Vulcanized Rubber," by L. Mullins.

On page 1037, Table 1 gives the composition of the base mixture used in the work. The parts by weight of smoked sheet rubber is given as 300, whereas it should be 100, *i.e.*, the composition should be:

| | |
|---|---|
| Smoked sheet rubber | 100 |
| Zinc oxide | 5 |
| Stearic acid | 2 |
| Sulfur | 3 |
| Mercaptobenzothiazole | 0.8 |

This error appeared in the April 1949 issue of the *India Rubber World*, from which the version in RUBBER CHEMISTRY AND TECHNOLOGY was reprinted. The same paper, which subsequently appeared in the *Proceedings of the Second Rubber Technology Conference*, London, June 23–25, 1948, contains the correct 100 parts by weight.

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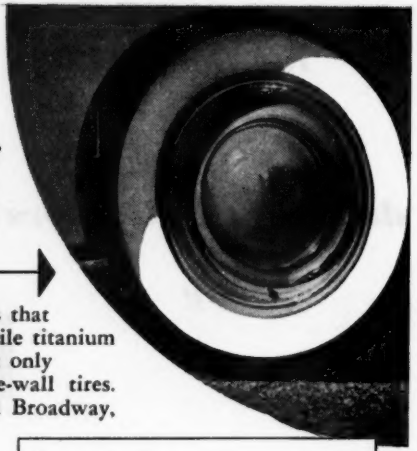

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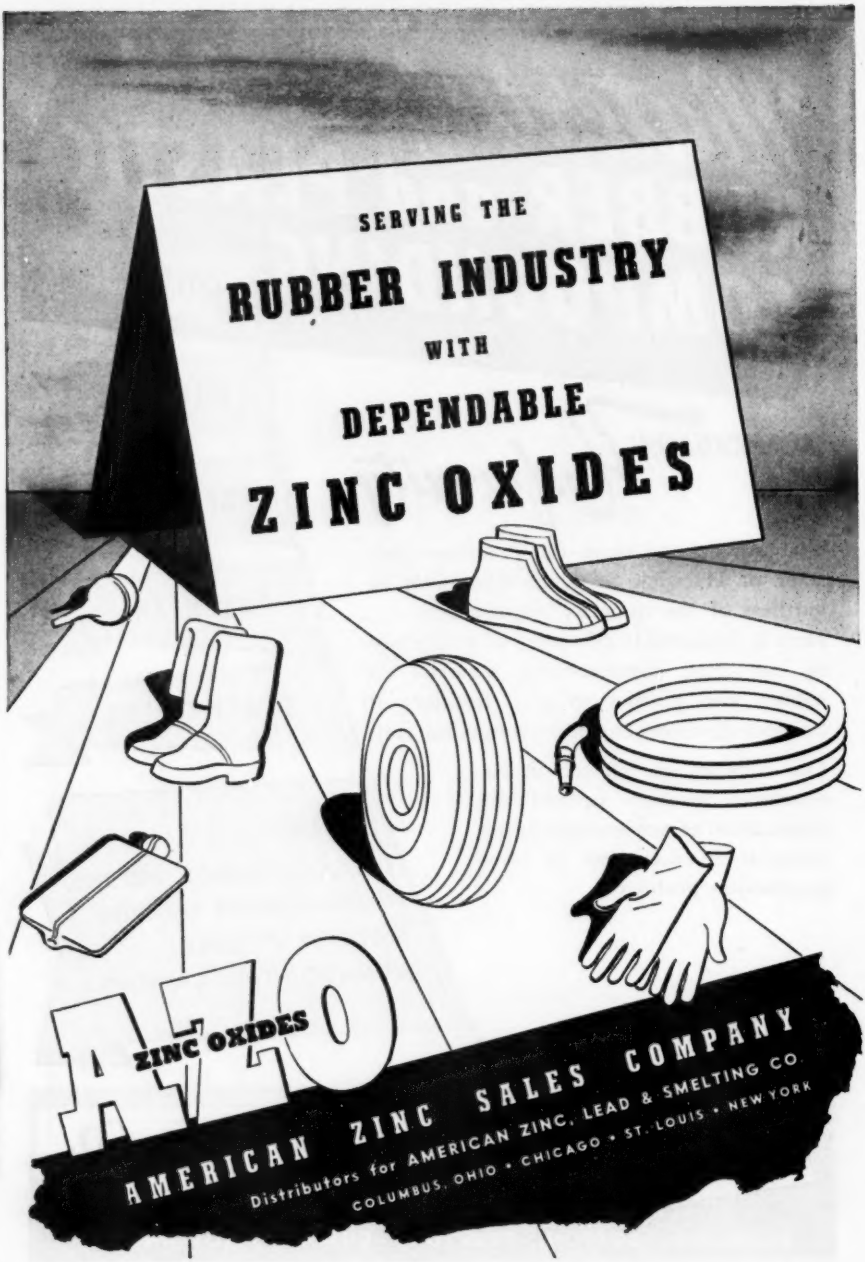
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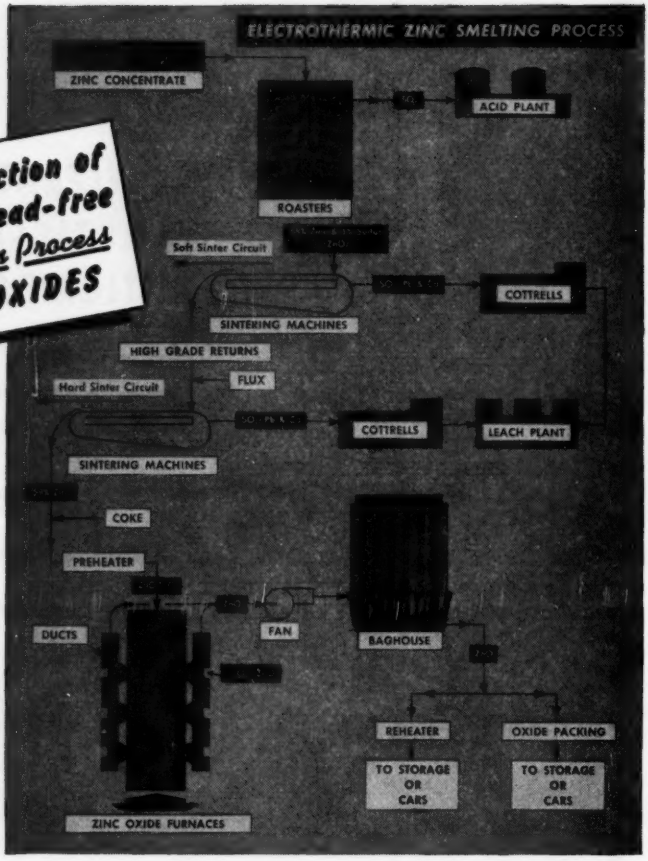


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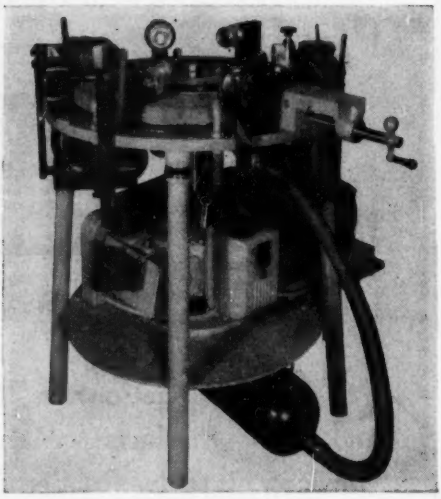

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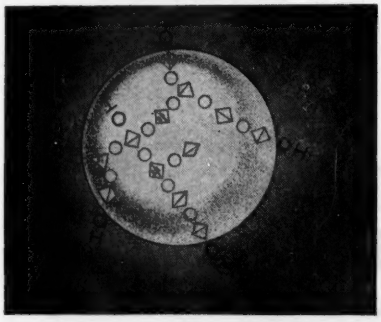

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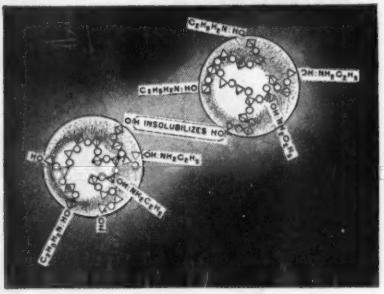


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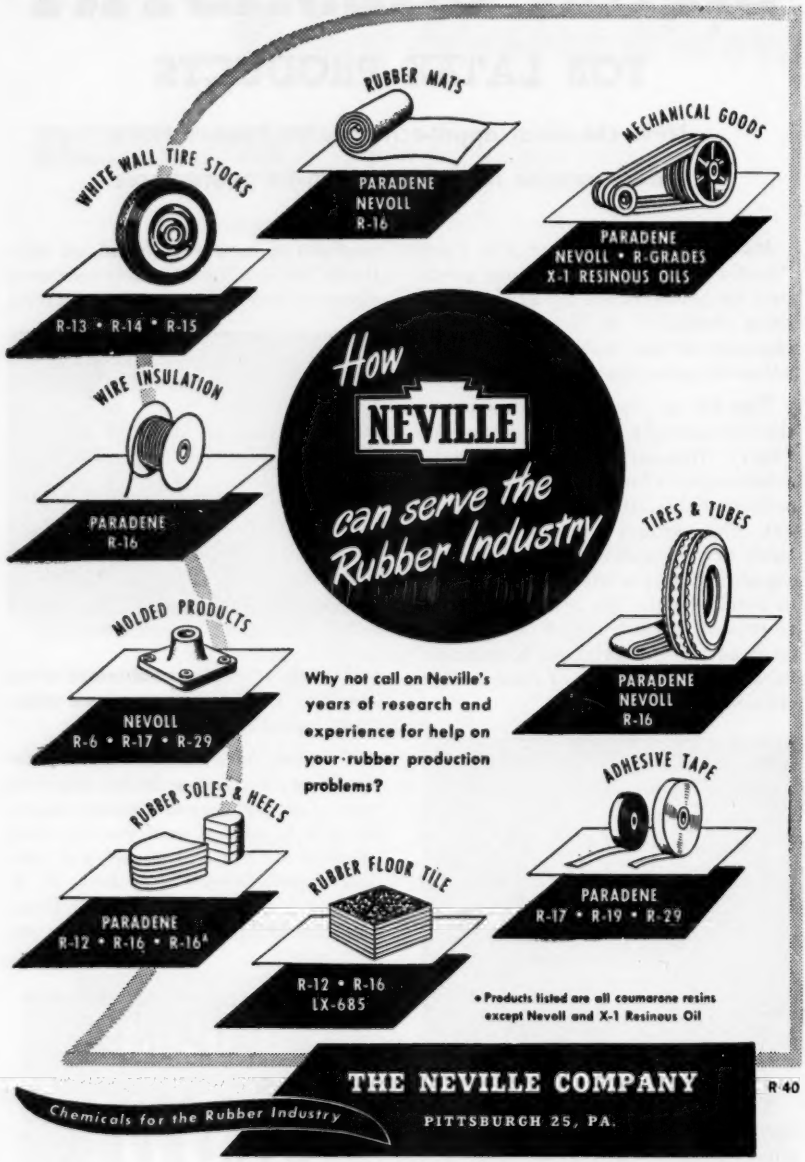
RUBBER MATS
PARADENE
NEVOLL
R-16
MECHANICAL GOODS
PARADENE
NEVOLL • R-GRADES
X-1 RESINOUS OILS
WHITE WALL TIRE STOCKS
R-13 • R-14 • R-15
How
NEVILLE
can serve the
Rubber Industry
WIRE INSULATION
PARADENE
R-16
TIRES & TUBES
PARADENE
NEVOLL
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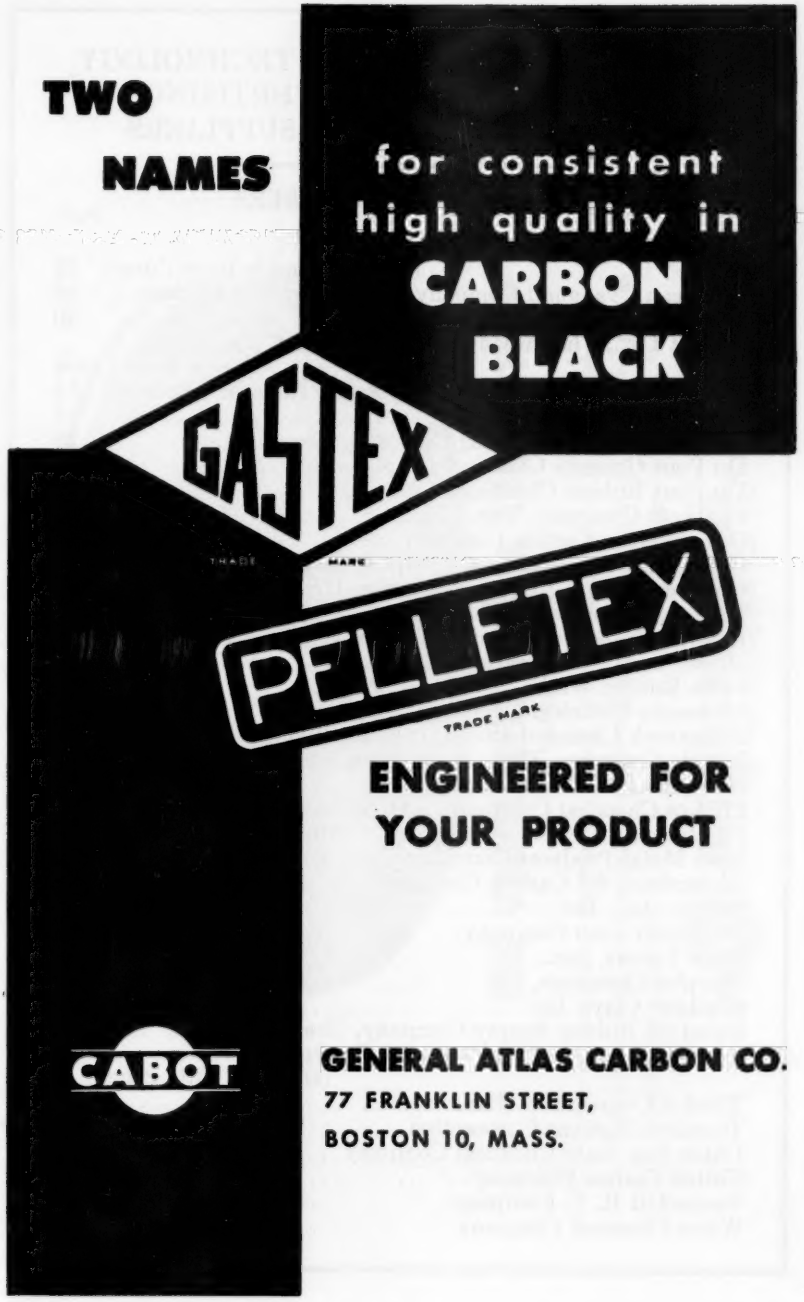
Why not call on Neville's years of research and experience for help on your rubber production problems?
ADHESIVE TAPE
PARADENE
R-17 • R-19 • R-29
RUBBER SOLES & HEELS
PARADENE
R-12 • R-16 • R-16*
RUBBER FLOOR TILE
R-12 • R-16
LX-685
• Products listed are all coumarone resins except Nevoll and X-1 Resinous Oil
THE NEVILLE COMPANY
Chemicals for the Rubber Industry
PITTSBURGH 25, PA.
R-40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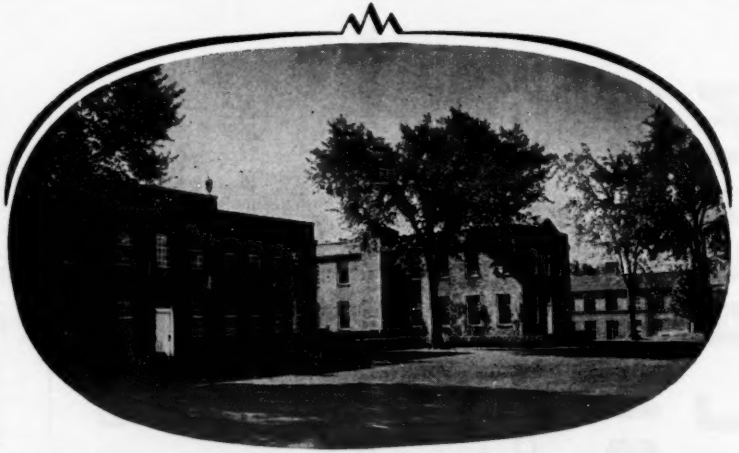

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# VINYL RESIN STABILIZERS

## To Protect Against HEAT *and* LIGHT

*For Process Safety and Satisfactory Service, use our Stabilizers*

**#3, #52, #21, V-1-N, JCX**

**VL-3, L paste, E6B**

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# RECIPE

from the Barrett Rubber Research Laboratory

FOR

# CUMAR*

## RESIN, LIGHT EX GRADE,

in Natural Rubber

The reinforcing and extending properties of "CUMAR" resin, light EX grade, promote quality along with economy in the design of molded and extruded natural rubber products. Its reinforcing character modifies the nerve of the rubber, thereby minimizing shrinkage and improving processing and calendering properties. It is particularly effective in the production of extruded items where reinforcement is essential in preventing sagging and flattening in open steam and air cures. As an extender for natural rubber, "CUMAR" resin, light EX grade, permits high filler loading while maintaining quality. It is especially useful for improving tear resistance. Its application is in automotive and aeronautical parts, mechanical and proofed goods, flooring, matting, bumper and channel stocks, and in items which are to be used in contact with dark colored enamels and lacquers.

## RECIPE

| | |
|---|---|
| Smoked Sheets | 100.00 |
| CUMAR* Resin, Light EX Grade | 18.00 |
| "DIXIE" Clay | 75.00 |
| Calcium Carbonate (Precipitated) | 75.00 |
| "SILENE" EF | 25.00 |
| Zinc Oxide | 5.00 |
| Stearic Acid | 2.00 |
| "ACERITE" Alba | 1.00 |
| Paraffin | 1.00 |
| Red Oxide | 5.00 |
| Sulfur | 3.75 |
| Benzothiazyl Disulfide | 1.25 |
| DOTG | 0.40 |
| Total | 309.40 |
| Specific Gravity | 1.55 |
| Rubber Hydrocarbon, % by weight | 32.4 |
| Rubber Hydrocarbon, % by volume | 54.4 |
| Mooney Viscosity, ML 4 min. @ 212 F. | 54 |
| Scorch Test Press Cures @ 250 F. | |

| Minutes | Cure |
|---|---|
| 5 | None |
| 10 | None |
| 15 | Slight |
| 20 | Fair |

Press Cure at 316 F. (70 lb.)—10 Minutes

| Tension and Hardness Data | Unaged | Aged 24 hrs. @ 100 C. |
|---|---|---|
| Stress, 300%, Psi. | 900 | 1000 |
| Tensile, Psi. | 1600 | 1250 |
| Elongation, % | 510 | 420 |
| Hardness, Shore A | 78 | 81 |
| Tear Resistance, Angle, Pounds Per One Inch Thickness | 135 | 145 |
| Press Cure at 316 F. (70 lb.)—18 Minutes | | |
| Abrasion Resistance, Du Pont | 375 | 340 |
| Compression Set, 25% Constant Deflection, % | 52.6 | — |
| Resilience, Yerzley, 20% Deformation, % | 45 | 36 |
| Rebound, Goodyear-Healey, % | 51.0 | 47.3 |
| Contact Stain (24 Hours @ 175 ± 2 F.) | Slight | |
| Migration Stain (24 Hours @ 125 ± 2 F.) | Slight | |

Barrett*


**THE BARRETT DIVISION**

ALLIED CHEMICAL & DYE CORPORATION

40 Rector Street, New York 6, N. Y.

In Canada: The Barrett Company, Ltd.

5551 St. Hubert St., Montreal, P.Q.

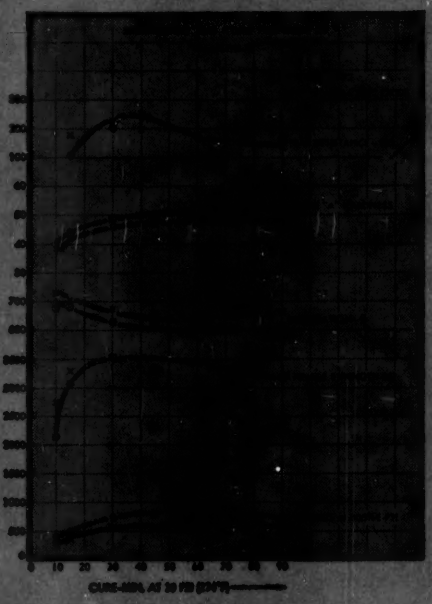

*Reg. U. S. Pat. Off.

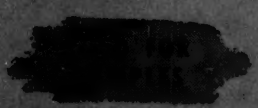
# AMONG WHITE PIGMENTS

# NEW ALBALITH-73

(LITHOPONE)

## OUTSTANDING FOR REINFORCEMENT





**Place Albalith-73** in your top group of white pigments for reinforcement — particularly for high tensiles and tear resistance.

**Albalith-73** is a special, surface-treated lithopone processed to give better dispersion and fewer aggregates in rubber. Its greater surface area in contact with rubber produces higher tensiles and tear resistance.

**Albalith-73** compares favorably with Protox-166 Zinc Oxide*, for example, in tensiles and tear resistance — although it of course does not activate accelerators. See accompanying stress-strain chart.

Compare **Albalith-73** with Zinc Oxide and other white pigments for reinforcement in your compounds now.

COMPOUND

| | |
|---|---|
| Smoked Sheet | 100 |
| Sulfur | 3 |
| MBT | 1 |
| Stearic Reactor | 1 |
| Stearic Acid | 3 |
| Protox-166 | 100- 0 |
| Lithopone | 0-70.6 |

*U.S. Patents 2,303,339 and 2,303,340

[redacted] JERSEY ZINC COMPANY

[redacted] VORK 7, N. Y.